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DEVELOPMENT OF ORGANIC SEALANTS FOR APPLICATIONS AT VERY LOW TEMPERATURES

Final Report

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CULVER CITY, CALIFORNIA

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MATERIALS TECHNOLOGY DEPARTMENT

Culver City, California

DEVELOPMENT OF ORGANIC SEALANTS  
FOR APPLICATIONS AT VERY  
LOW TEMPERATURES \*

by

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30 June, 1962

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\* Final Report Covering the  
Period 1 July 1961 to 30 June 1962

( NASA Contract No. NAS 8-2428 )

George C. Marshall Space Flight Center,  
NASA, Huntsville, Alabama

Approved: W. H. Colner  
Manager, Materials Technology Department



## FOREWORD

This report was prepared by the Hughes Aircraft Company to cover the work completed during the period 1 July 1961 to 30 June 1962 under a contract for the development of sealant materials for use in the extremely cold environments of launch vehicles. This contract is sponsored by the George C. Marshall Space Flight Center, NASA, Huntsville, Alabama, with Clyde M. Holmes as Project Engineer.

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## ABSTRACT

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During the first year of this contract commercially available sealants were screened to determine their suitability as cryogenic sealants. The most promising materials, Adiprene L-100, cured with castor oil, and a silicone sealant XE-1027 were modified to increase their ability to withstand stresses at liquid nitrogen temperature. Further evaluation studies indicated that the Adiprene formulation reinforced with glass fabric resists thermal shock, bending and vibration loads at 76°K, and has a coefficient of thermal contraction approximately equal to that of aluminum. Silicone polymers were synthesized that may serve as bases for sealants having improved low temperature flexibility. A fixture was designed and used for the testing of sealants vibrated at cryogenic temperatures. A sealant was formulated and evaluated for the sealing of crevices in cryogenic propellant dome tanks. A literature survey is included in the report.

AUTHOR

## INTRODUCTION

The purpose of this program is to develop sealants and seal materials for launch vehicle use in extremely low temperature environments. Sealants are defined here as curable elastomers applied by brush, spatula, or caulking gun, and seal materials as cured gaskets or O-rings. The low temperatures encountered are produced by cryogenic fluids used as vehicle propellants.

Curable sealants will serve to provide a field repair of propellant tanks and lines that would otherwise require extensive and time consuming repairs. Ideally, the sealants and seal materials must retain a measure of flexibility or toughness at temperatures down to 20°K, roughly the boiling point of liquid hydrogen. However, materials of considerable utility will be developed if adhesion to metal substrates and resistance to bend loading and shock and vibration can be achieved at 76°K.

In developing an organic based sealant suitable for use at these temperatures, a thorough knowledge of the limitations of presently available curable elastomers is required. This knowledge can be based on observations of some physical properties exhibited by the elastomers at low temperatures. Although extreme flexibility in the cryogenic temperature range is beyond the capabilities of present commercially available materials, such observations may lead to a selection of polymer systems whose low temperature properties may be improved. Improvement may result from sealant formula modifications or by variations in the polymer structure.

The approach taken by the Hughes Aircraft Company, under this contract, was to screen polymer systems having the lowest possible glass transition temperature and the least tendency for crystallization, and to modify these polymers to achieve better low temperature properties through compounding modifications. In addition, new polymers whose molecular structures give promise of having better low temperature flexibility were synthesized.

The screening of existing materials and modified materials, for use as cryogenic sealants, consisted of measuring their flexibilities at



76°K and by observing their thermal contraction characteristics and volume changes down to 76°K. Not only must the sealants exhibit a degree of ductility or lack of brittleness at these temperatures, but their coefficients of thermal contraction should closely match those of the metal substrates, and volume changes at transition temperatures should be held to a minimum.

## INITIAL LITERATURE SURVEY

The existing information on the low temperature properties of polymeric materials, test methods, and fluid compatibility was gathered in an initial search of published papers and reports and through personal contacts. This information, as part of the contract, is reported here. A discussion of the problems is given first. In the References section of this report, most references have been abstracted to provide a more complete problem discussion.

### Discussion

The problem of providing seals for cryogenic liquid vessels and transfer equipment had in the past been successfully solved through the use of properly designed metallic joints. With the widespread use of cryogenics as liquid rocket propellants, however, new problems for dynamic as well as static conditions were encountered that required the use of sealant and seal materials compatible with the fluids and having enough resiliency, at these temperatures, to restrict fluid flow. Non-metallic materials commonly used for gaskets, O-rings, and lip seals were found to provide poor seals either because of brittleness or sensitivity to liquid oxygen.

Fluorocarbon elastomers have recently been successfully used in all but the most severe dynamic conditions. Teflon as an O-ring and gasket material will retain some measure of resiliency down to liquid hydrogen temperatures, and if compressed sufficiently at room temperature, will maintain seals down to 20°K.<sup>(1)(2)(3)(4)</sup> In some instances where flexibility and liquid oxygen resistance is not of importance, natural rubbers, Hypalon, Viton A, and Neoprene have all been found to be satisfactory as static seals. It is important to note here, however, that a high degree of compression at room temperature must be imparted to these seals (60%-80%). The greater contraction of the elastomers, with less initial compression, is enough to allow leakage under vacuum loading.<sup>(1)</sup> Thus these elastomers are adequate because

of their compression properties, their high crush strength, and their lack of failure under high pre-load.

Metallic seals, such as hollow stainless steel O-rings, are being used by the manufacturers of cryogenic storage and handling equipment. Soft metal facings on stainless steel gaskets have proved to be adequate for many specialized equipment seals. Indium, lead, silver and aluminum have all been successfully used.<sup>(5)(6)(7)</sup> A new concept of seal manufacture utilizes a sintered stainless steel fiber body, impregnated either with softer metals or with phenolic resins.<sup>(5)</sup> The metal fiber "mesh" maintains resiliency, while the softer component will conform to the substrate faying surfaces.

Seal materials have thus been developed and used with moderate success. The task of developing a readily usable sealant is a more difficult problem at this time, because of the nature of materials that must be used in its manufacture. Curable organic systems must be used and adhesion to the metal substrates is of utmost importance. Because of the dimensional changes associated with elastomer crystallization and their relatively high coefficient of thermal contraction, modifications must be made in the polymers, to reduce the degree of crystallization and in the compounded sealant.<sup>(8)(9)(10)</sup>

Ideally, elastomers for use at cryogenic temperatures, should have a glass transition temperature and crystallization temperature so low that they remain quite flexible during service.

These elastomers are not yet available, fluorocarbons being the only known materials of this nature that retain as much as 6-8% elongation at 20°K.<sup>(11)(12)</sup> It could be possible, however, to develop new polymers, control the crystallinity of present polymers, or modify polymer systems to develop a toughness or resiliency necessary to withstand moderate stresses.

A reduction in the coefficient of thermal expansion will be necessary to reduce the thermal stresses at the sealant-substrate interface. This may be accomplished through the use of low coefficient fillers.<sup>(13)(14)</sup>

A number of elastomers have been mentioned as having low temperature properties that make them appear attractive as a sealant matrix.

Fluorinated silicones, cyanosilicones, perfluoronitroso elastomers will merit considerable attention.<sup>(15)(16)</sup> Added low temperature resistance is usually imparted to silicone formulations by the introduction of functional groups other than methyl in the siloxane backbone; this has usually been one or two phenyl groups. The crystallization temperatures and the amount of crystallization are lower than for the dimethylsiloxane.<sup>(8)(11)(15)</sup>

Some newer polyurethane formulations, although showing a marked decrease in flexibility below -100°F, have excellent adhesion to metallic surfaces. They could conceivably be useful if properly compounded.<sup>(17)(18)</sup>

Epoxy resins, as formulated in structural adhesives, retain excellent lap shear strength at temperatures down to 20°K.<sup>(19)(20)</sup> These tests, however, were under static conditions and their crystallization and glass transition temperatures are well above the cryogenic range. As formulation constituents, their excellent adhesive properties may be used to improve this property in other elastomers.

Polysulfide rubber polymers, although having brittle points above the proposed operating range of a cryogenic sealant, may well be considered as a matrix constituent. For example, ease of cure, adhesion to metal substrates, and resistance to hydrocarbon fluids may improve these properties in polyurethane systems.<sup>(21)</sup>

Of the polymer systems referred to as "rubbers", the materials considered to hold the greatest promise in this field are the polybutadienes. The carboxyl terminated butadienes can be cured to a rubber by terminal chain extension, and the amount of cross-linking from the double bonds can be controlled by varying the amounts of suitable catalysts. Thus many of its physical properties, perhaps extending below its glass transition point, can be controlled.<sup>(21)</sup> Combinations of the cis and trans butadiene isomers can be blended to give cured formulations with a highly unordered molecular structure. Crystallization is therefore sharply reduced. From preliminary observations, a ratio of 80 parts cis to 20 parts trans appears to give a product having the least amount of crystallization.<sup>(22)</sup>

Two or more mutually incompatible or partially compatible polymers can be combined in a process usually referred to as "polyblending". An

example of this process is the combination of polystyrene and GRS rubber to form a product having a higher impact resistance than either of its parent members. Such a product, instead of having a sharply defined glass transition region, usually has a much broader temperature range in which it maintains a more leathery character.<sup>(21)</sup> This technique may be used to extend the temperature range in which a polymer system retains a measure of resiliency.

Useful methods of testing for the determination of low temperature properties of polymers include retraction studies as a measure of crystallinity<sup>(23)(24)</sup>, the Gehman torsional modules test, and the Brittle Point Test<sup>(24)</sup>. Seal materials, such as gaskets, can be conveniently evaluated between two flanges either in a vacuum pressurized apparatus or a positive pressure apparatus<sup>(1)(4)(25)</sup>. An apparatus is available for the measurement of shear modulus and internal friction<sup>(26)</sup>.



## EVALUATION OF EXISTING MATERIALS

The initial development phase of the program was concerned with the testing and evaluation of those presently available curable elastomers felt to be the most promising candidates for further modification.

The first screening test chosen for the ranking of sealants was a low temperature flexibility test, at 76°K, of aluminum strips coated with the sealants. Further suitability tests were made by studying the thermal contraction properties of the best materials as determined by the flexibility tests.

### Low Temperature Flexibility

The sealants, or curable elastomers, tested are listed in Table I. They were applied as a nominal 1/16 inch thick coating to strips of 0.032 x 1 x 6 inch 2024-T3 aluminum alloy and cured according to the manufacturers' recommendations. In instances where a primer is suggested to promote adhesion, it has been used.

The aluminum surfaces were prepared by immersing the strips in a mixture of 30 parts of water, by weight, 4 parts concentrated sulfuric acid, by weight, and 1 part sodium dichromate, by weight. After being etched in this solution for 10 minutes, at 140-160°F, the strips were rinsed in distilled water, air dried and wrapped to prevent surface contamination.

The low temperature flexibility apparatus, described in MIL-S-8516 and modified by the addition of insulated walls, was used to bend the coated aluminum strips around a 2 inch diameter mandrel. It is schematically shown in Figures 1 and 2.

The entire apparatus was cooled first with dry ice and then with liquid nitrogen. The specimens were then inserted and liquid nitrogen was allowed to flow over them for approximately one minute before testing. Figure 3 shows the flexibility test in operation. Photographs of representative specimens, after test, are shown in Figure 4 for each sealant.

FN*	Product Designation	Type
1	3 M's EC-1942	Polymer "B" base (proprietary)
2	3 M's EC-1946	Polymer "B" base (proprietary)
3	3 M's XS-1168521	Polymer "B" base (proprietary)
4	3 M's EC-1675	Polysulfide base
5	3 M's EC-1239	Polysulfide base
6	3 M's SF-50 film	Polysulfide base
7	3 M's EC-1667	Silicone base
8	3 M's EC-2186	Epoxy base
9	3 M's XD-976651	Epoxy base
10	3 M's XD-1087747	Epoxy base
11	Thiokol Chemical Corporation's LP-205 LP-370 LP-33	Butyl formal, butyl ether, and polysulfide blend
12	Thiokol Chemical Corporation's ZL-434 Tipox B	Carboxyl terminated polybutadiene and epoxy blend
13	DuPont's Adiprene L-100 cured with castor oil Chemlok 607 primer	Polyurethane base
14	General Electric's RTV-X77 Chemlok 607 primer	Silicone base
15	General Electric's XE-1027 Chemlok 607 primer	Silicone base
16	Coast Proseal Company's Proseal 786	Polyurethane base
17	Coast Proseal Company's Proseal 777	Polyurethane base
18	Emerson and Cuming's Eccosil 4712 Chemlok 607 primer	Epoxy-silicone base
*FN = Formulation number.		

Table I. Sealant formulations screened.

FN*	Product Designation	Type
19	Product Research Company's PR 1527 Chemlok 607 primer	Polyurethane base
20	Dow Corning's RTV 5302 and RTV 5303 Chemlok 607 primer	Silicone base
21	Dow Corning's Q2-0046 Chemlok 607 primer	Silicone base
22	Dow Corning's Q-9-0002 Chemlok 607 primer	Silicone base
23	Dow Corning's Q-3-0121 Chemlok 607 primer	Silicone base
24	Dow Corning's Q-9-0031 Chemlok 607 primer	Silicone base
25	Dow Corning's Q-9-0006 Chemlok 607 primer	Silicone base
26	Dow Corning's Silastic LS-53 A-4094 primer	Fluorosilicone base
27	Dow Corning's Silastic LS-63 A-4094 primer	Fluorosilicone base
28	Dow Corning's Silastic 651 Chemlok 607 primer	Silicone base
29	Dow Corning's Silastic 675 Chemlok 607 primer	Silicone base
30	Dow Corning's Silastic 52 Chemlok 607 primer	Silicone base
31	Dow Corning's Silastic 82 Chemlok 607 primer	Silicone base
32	Dow Corning's Silastic S-2096 Chemlok 607 primer	Silicone base
*FN = Formulation number.		

Table I (continued).

FN*	Product Designation	Type
33	Dow Corning's Silastic S-2097 Chemlok 607 primer	Silicone base
34	Dow Corning's Silastic 916 A-4094 primer	Silicone base
35	North American Aviation's NA 1069-266 Sealant Chemlok 607 primer	Proprietary
*FN = Formulation number.		

Table I (continued).

Brittle failure was exhibited by all materials, showing that, at temperatures down to 76°K, the stresses imposed upon these materials by the bending are sufficient to crack them and cause loss of adhesion. The important consideration here, however, is not whether a sealant passes or fails this test, but how it reacts to the stress. The test is most severe and it is doubtful that any existing sealant, without considerable reinforcement, will show enough strength and flexibility to be bent to this degree and not break. But the mode of failure does suggest that some polymers are not as brittle as others and have promise as a basis for further modifications.

Two sealants, Du Pont's Adiprene L-100 cured with castor oil and General Electric's one component XE-1027, were shown to have the most flexibility or toughness at 76°K and were subsequently used as the basis for modified sealants. Minnesota Mining and Manufacturing Company's EC 1667 and Coast Proseal's 777 also showed promise and the modification improvements, specifically for cryogenic service can be applied to them.

These materials were prepared and cured as follows:

Material	Cure
Adiprene L-100            100 pbw Castor oil                36 pbw Chemlok 607 primer	Primer applied by brush and dried at room temperature for 30 minutes Mixing temperature - 250°F Cure: 285°F for 3 hours
EC 1667                    100 pbw Accelerator                10 pbw	Cure: room temperature overnight, then 160°F for 2 hours
XE 1027 (one component) Chemlok 607 primer	Primer applied by brush and dried at room temperature for 30 minutes Cure: 200°F overnight
Proseal 777                100 pbw Catalyst                    8.4 pbw	Cure: 150°F for 3 hours



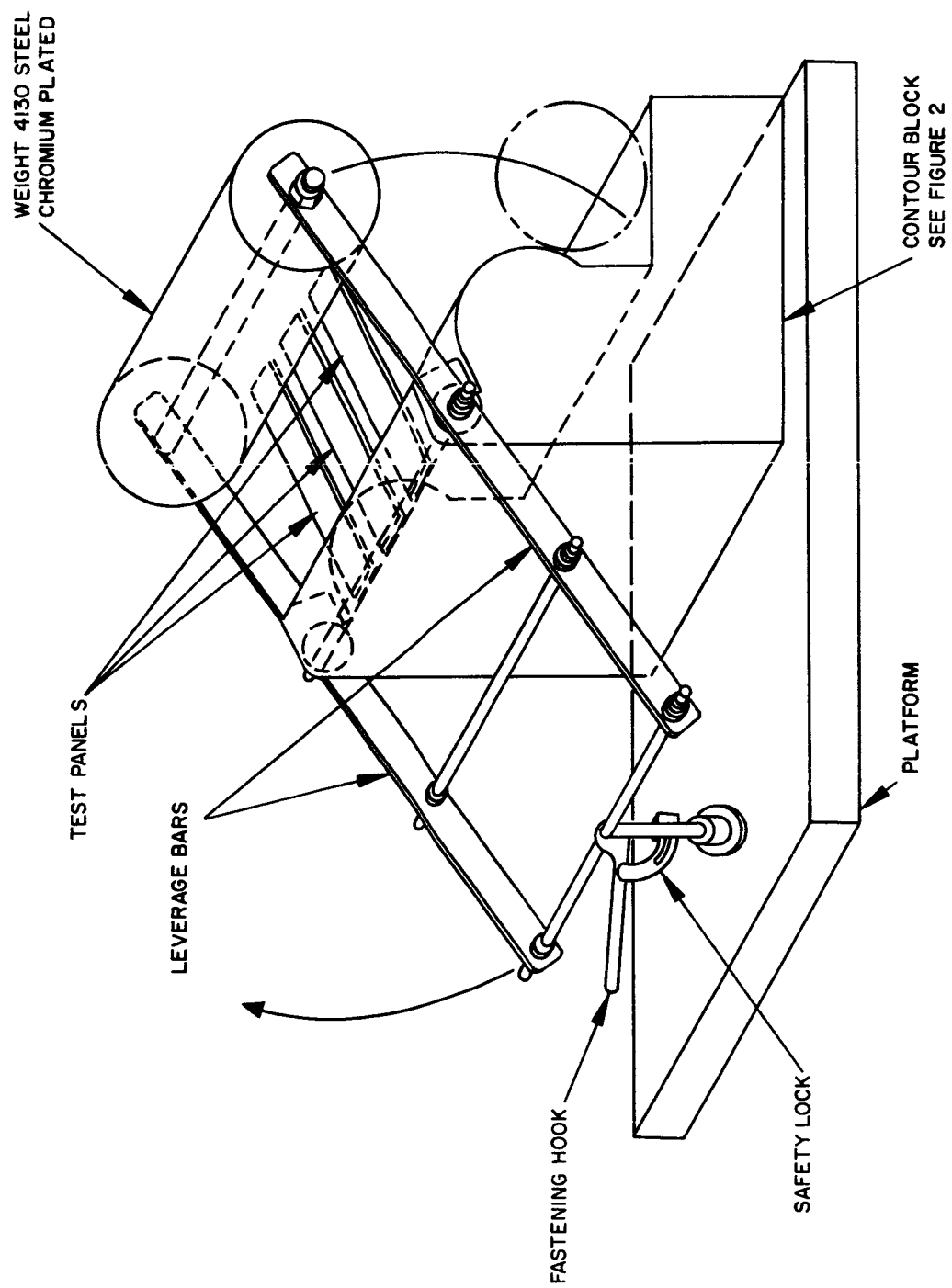


FIGURE 1 LOW TEMPERATURE FLEXIBILITY TEST

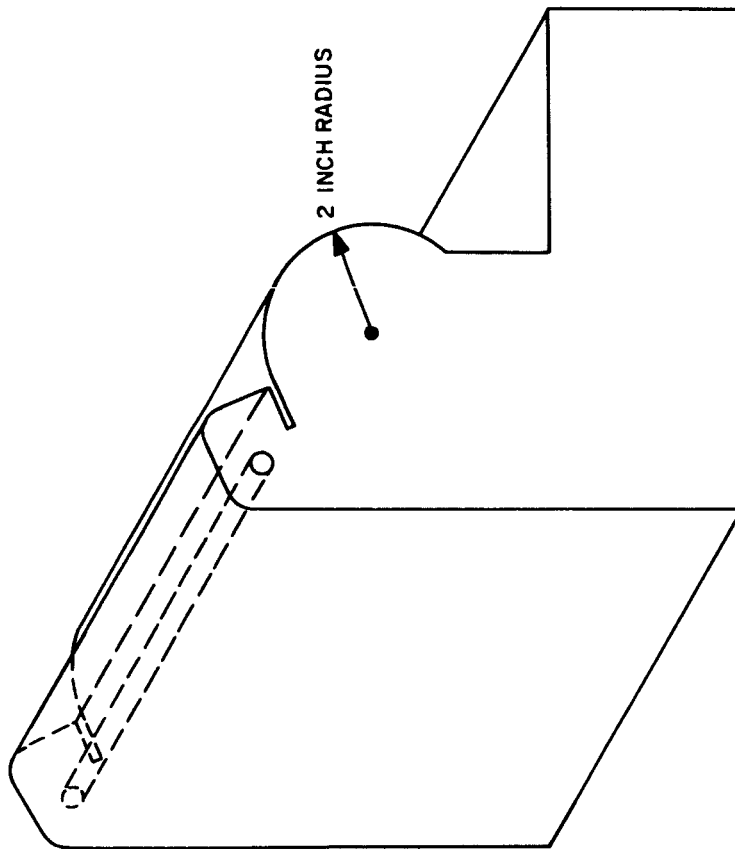


FIGURE 2 LOW TEMPERATURE FLEXIBILITY TEST BLOCK

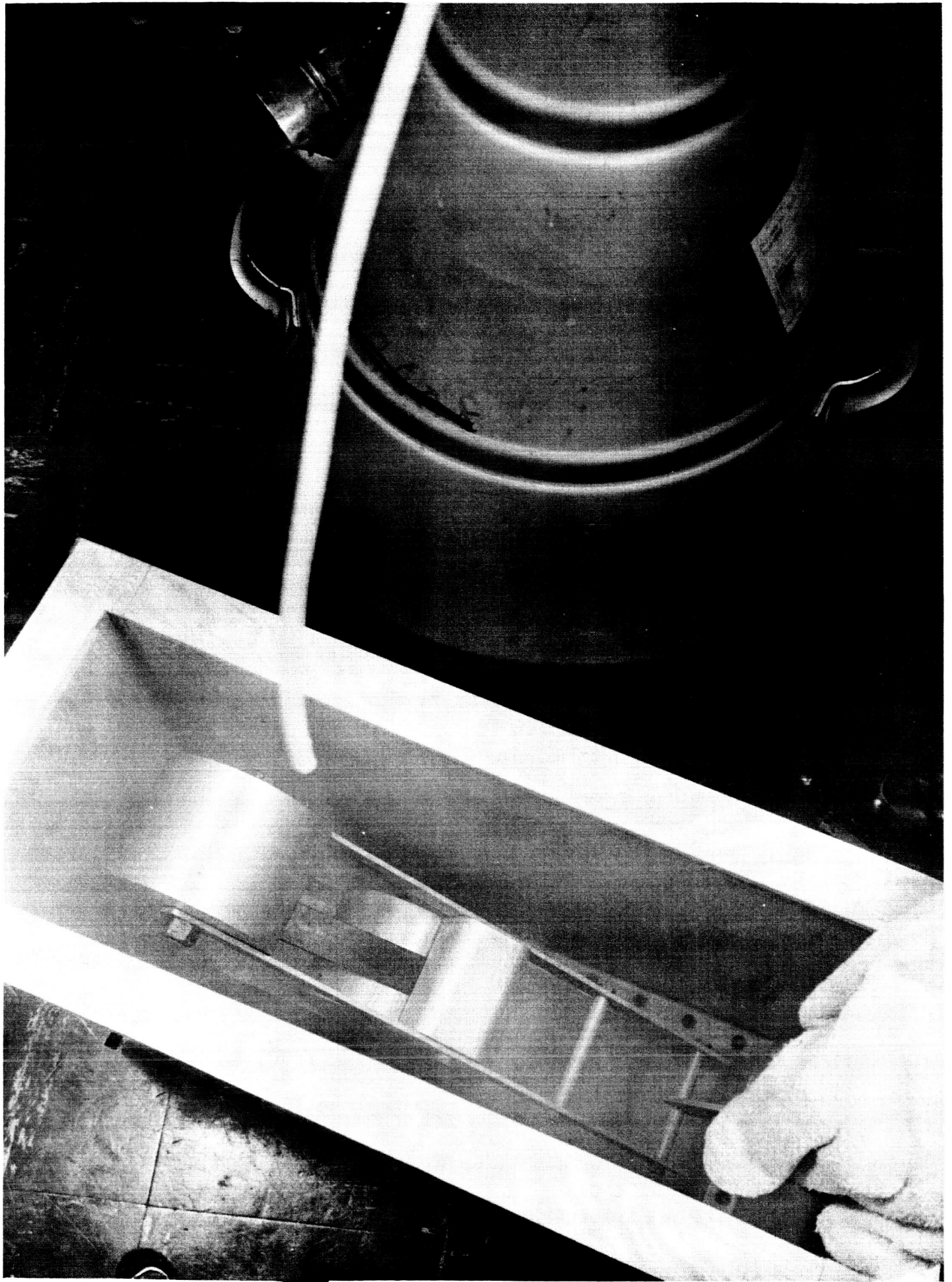


FIGURE 3 OPERATION OF LOW TEMPERATURE FLEXIBILITY TEST

FIGURE 4



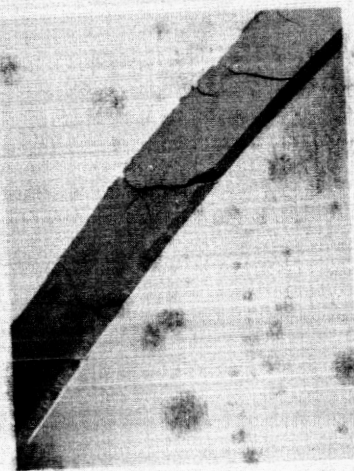
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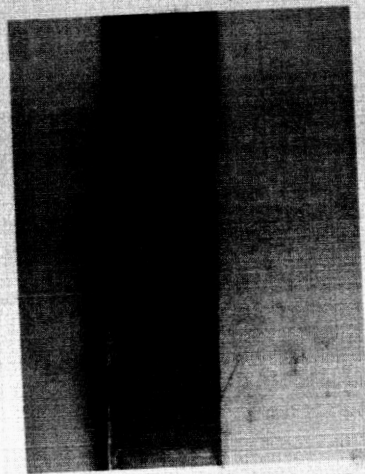
Formulation 2



Formulation 3



Formulation 4



Formulation 5



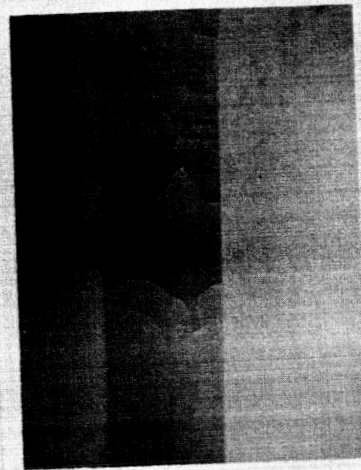
Formulation 6



Formulation 7



Formulation 8



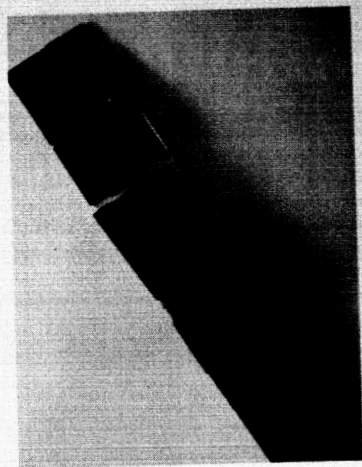
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FIGURE 4 (cont'd)



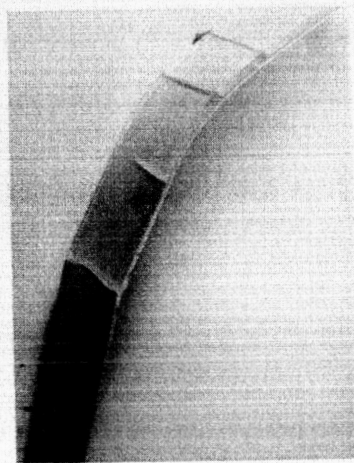
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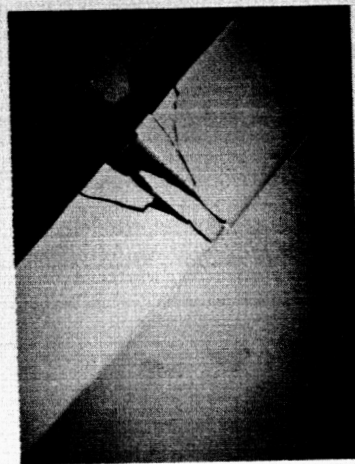
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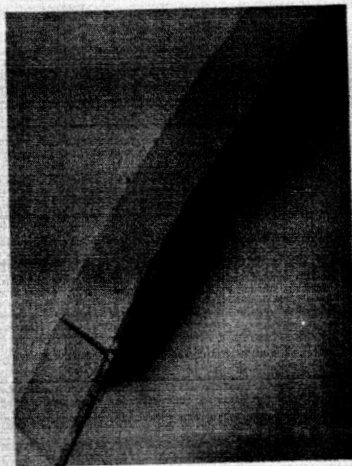
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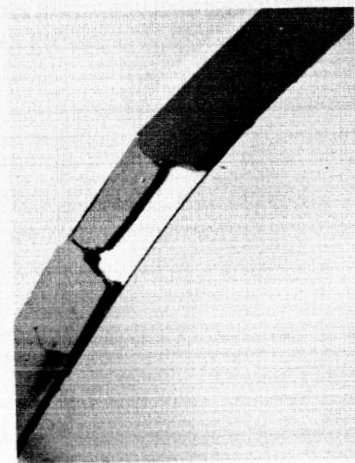
Formulation 13



Formulation 14



Formulation 15



Formulation 16



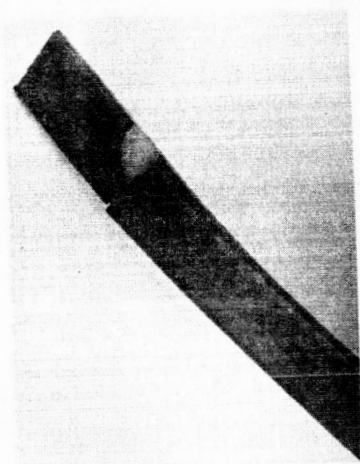
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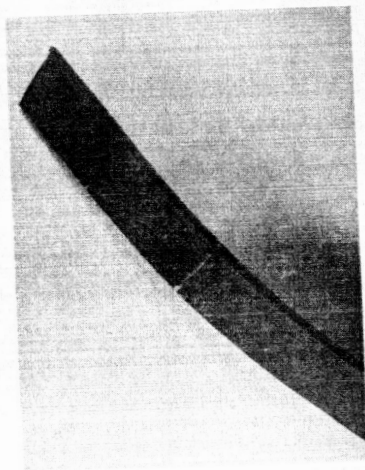
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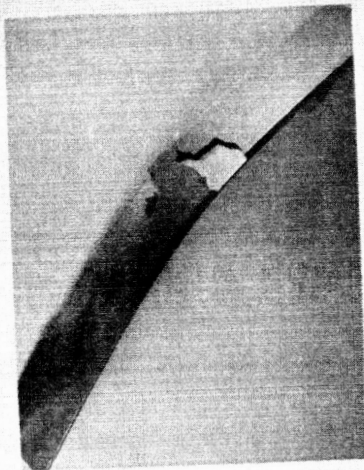
FIGURE 4 (cont'd)



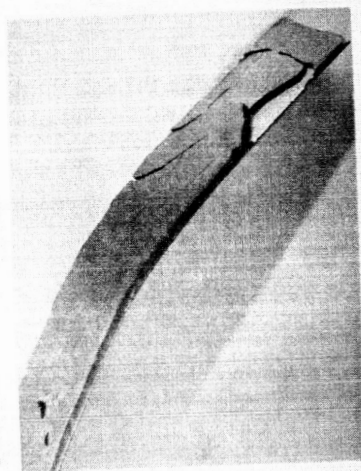
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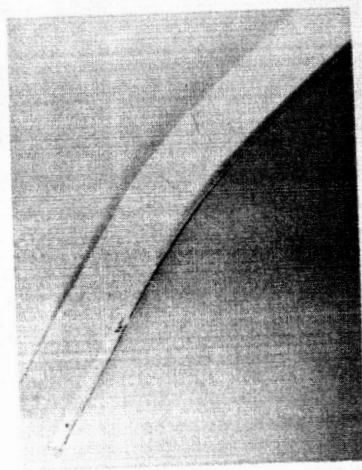
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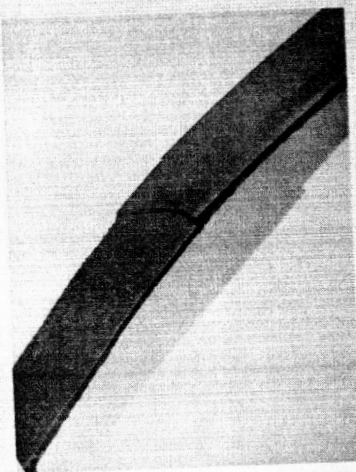
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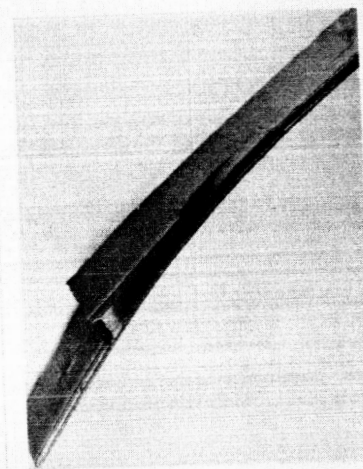
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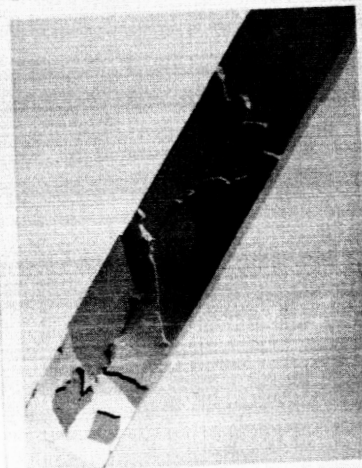
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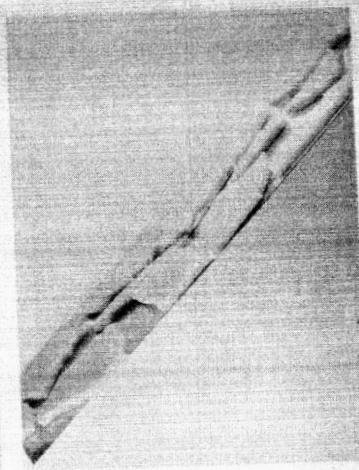
Formulation 24



Formulation 25

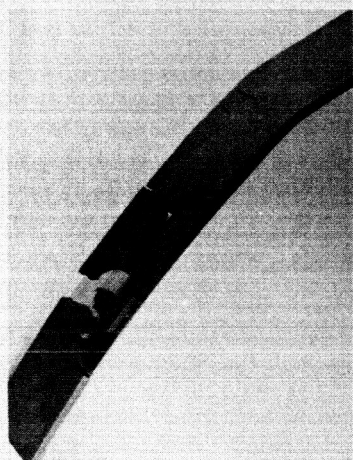


Formulation 26

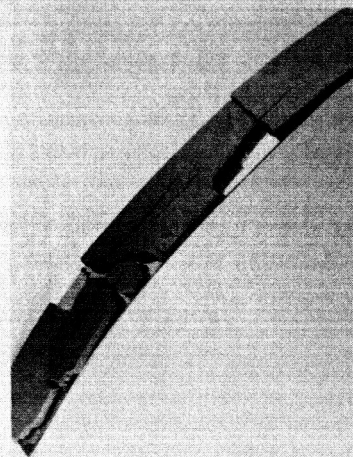


Formulation 27

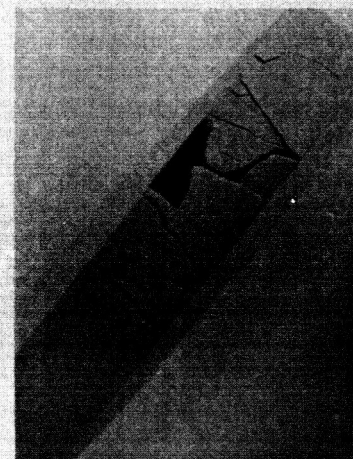
FIGURE 4 (cont'd)



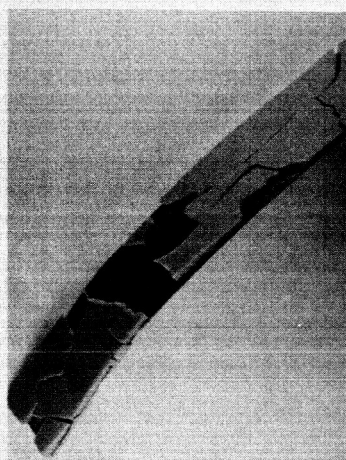
Formulation 28



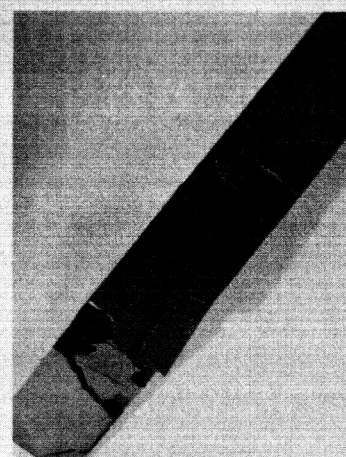
Formulation 29



Formulation 30



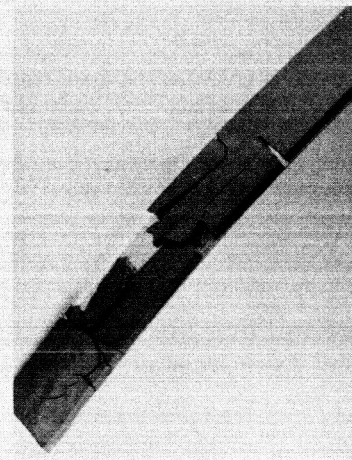
Formulation 31



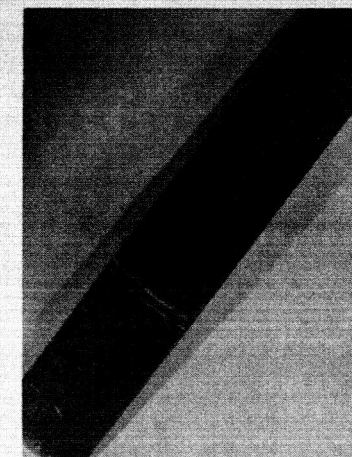
Formulation 32



Formulation 33



Formulation 34



Formulation 35

## SEALANT MODIFICATION

The Adiprene L-100 was modified by compounding it with a variety of reinforcing fillers and curing agents. The purpose of this work was twofold, to increase its low temperature bend strength at 76°K and to reduce the overall coefficient of linear contraction to match, as closely as possible, that of the metal substrate. It was found that glass fabric applied as reinforcement to the Adiprene L-100 castor oil mixture did allow the coated aluminum specimens to be bent around the two inch diameter mandrel with no discernible cracks or ruptures. More plies of the 112 fabric were required than the 181 style fabric to achieve the same degree of reinforcement. Therefore, repeated tests were conducted using six plies of the 181 fabric in a nominal 1/16 inch coating as a standard.

The XE-1027 silicone sealant was also reinforced in this manner with similar results.

At this point in the program, thermal contraction studies on the Adiprene and the EC 1667 indicated a preference for the polyurethane elastomers over the available silicones. The EC 1667 exhibited a large volume change at its crystallization temperature characteristic of present silicone elastomers and the remaining modification efforts were devoted to the Adiprene L-100. Volume changes during cool-down where the sealant may remain near its crystallization temperature for an appreciable length of time, will cause additional stresses at the sealant-metal interface. This work is discussed later in the report.

The formulations used are given in Table II, and photographs of representative bend specimens, after testing at liquid nitrogen temperature, are shown in Figure 4A. Although a single sealant material, i.e., one with the reinforcing filler in the resin before application, is more desirable, the Adiprene L-100 glass fabric "system" gives promise of meeting the proposed sealant requirements. Note that specimens were tested in which various reinforcements were added to

the uncured elastomers before application. In such cases, apparently the fibers or powders, because of their discontinuity, do not transfer loads to a high enough degree.

Various Buna N and stannosiloxane formulations were made and tested and are included in this modification section of the report.

FN*		FN*	
36	Adiprene L-100 100 gm. Castor oil 36 gm. 10 ply 112 glass fabric reinforcement Chemlok 607 primer	40	Adiprene L-100 100 gm. Castor oil 36 gm. Cab-o-Sil 1 gm. 1/2 x 1/2 in. square 112 glass cloth reinforcement 50 gm. Chemlok 607 primer
37	Adiprene L-100 100 gm. Castor oil 36 gm. 6 ply 181 glass fabric reinforcement Chemlok 607 primer	41	Adiprene L-100 100 gm. Castor oil 36 gm. Cab-o-Sil 1 gm. Woven glass roving reinforcement Chemlok 607 primer
38	Adiprene L-100 100 gm. Castor oil 36 gm. 1/4 inch milled glass fibers 10 gm. Chemlok 607 primer	42	Adiprene L-100 100 gm. Castor oil 36 gm. 3 ply Nylon Tricot reinforcement Chemlok 607 primer
39	Adiprene L-100 100 gm. Castor oil 36 gm. Glass wool 100 gm. Chemlok 607 primer	43	Adiprene L-100 100 gm. Castor oil 36 gm. 10 ply Dacron marquesette reinforcement Chemlok 607 primer
*FN Formulation Number			

Table II. Sealant formulation modifications.

FN*		FN*	
44	Adiprene L-100 100 gm. Castor oil 36 gm. 3 ply Dacron Tricot reinforcement Chemlok 607 primer	49	Adiprene L-100 100 gm. MOCA 11 gm. Flexol TOF 20 gm. Mono 90 filler 100 gm. Chemlok 607 primer
45	Adiprene L-100 100 gm. Castor oil 36 gm. 3 ply Nylon Tulle reinforcement Chemlok 607 primer	50	Adiprene L-100 100 gm. MOCA 11 gm. Flexol DOP 10 gm. Thermax 100 gm. Chemlok 607 primer
46	Adiprene L-100 100 gm. Castor oil 36 gm. Teflon felt approx. 1/8 in. Chemlok 607 primer	51	Adiprene L-100 100 gm. MOCA 11 gm. Flexol TOF 20 gm. Lithafrax 100 gm. Chemlok 607 primer
47	Adiprene L-100 100 gm. Castor oil 36 gm. Etched FEP Teflon powder 130 gm. Chemlok 607 primer	52	Adiprene L-100 100 gm. Castor oil 18 gm. 1,4- Butanediol 2.2 gm. Chemlok 607 primer
48	Adiprene L-100 100 gm. Castor oil 36 gm. Celluflex CEF 10 gm. Fused silica 100 gm. Chemlok 607 primer	53	G. E.'s XE-1027 (one component) 10 ply 112 glass fabric Chemlok 607 primer
*FN Formulation Number			

Table II. (continued).

FN*		FN*	
54	G.E.'s XE-1027 (one component) 6 ply 181 glass fabric Chemlok 607 primer	59	Paracril AJ gum stock (Buna N base) 100 gm. Zinc oxide 5 gm. Benzothiazyl disulfide 1 gm. Sulfur 2 gm. Asbestos 60 gm.
55	Paracril BJ LT gum stock 100 gm. (Buna N base) Zinc oxide 5 gm. Benzothiazyl disulfide 1 gm. Sulfur 2 gm. Asbestos 60 gm.	60	Polymer 4355-56 (Stanno-siloxane base) 100 gm. Paracril BJ LT 100 gm. Plastibest 120 gm. Bis silyl benzene 5 gm.
56	Paracril BJ LT gum 100 gm. Zinc oxide 5 gm. Benzothiazyl disulfide 1 gm. Sulfur 2 gm. Chemlok 607 primer	61	Polymer 4355-56 100 gm. Paracril D 100 gm. (Buna N base) Plastibest 120 gm. Bis silyl benzene 10 gm.
57	Paracril D 100 gm. Zinc oxide 5 gm. Benzothiazyl disulfide 1 gm. Sulfur 2 gm. Chemlok 607 primer	62	Polymer 4355-56 100 gm. Paracril AJ 100 gm. Plastibest 120 gm. Bis silyl benzene 5 gm.
58	Paracril D 100 gm. Zinc oxide 5 gm. Benzothiazyl disulfide 1 gm. Sulfur 2 gm. Asbestos 60 gm.		
*FN Formulation Number			

Table II (continued).



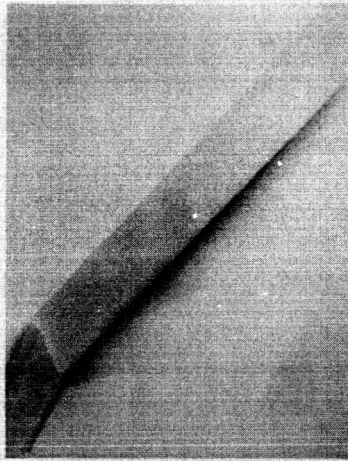
FIGURE 4A



Formulation 36



Formulation 37



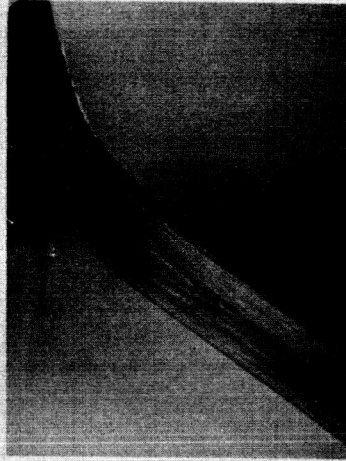
Formulation 38



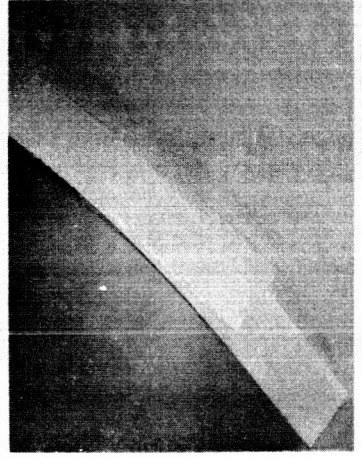
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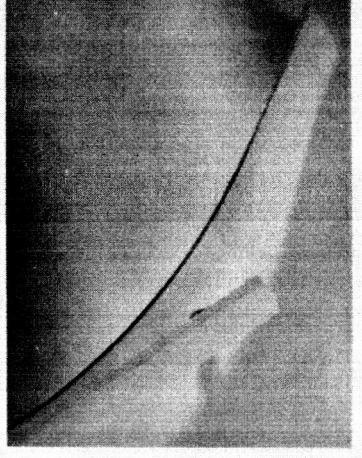
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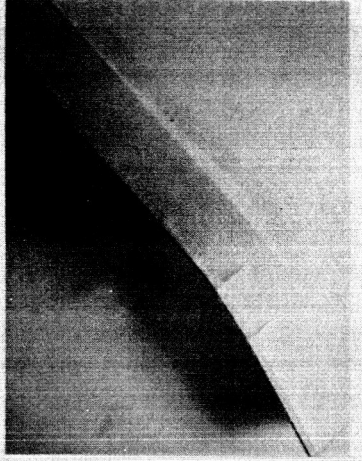
Formulation 41



Formulation 42



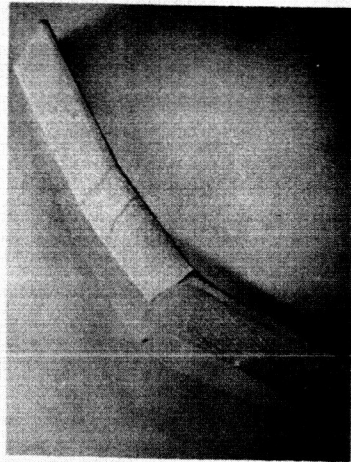
Formulation 43



Formulation 44



FIGURE 4A (cont'd)



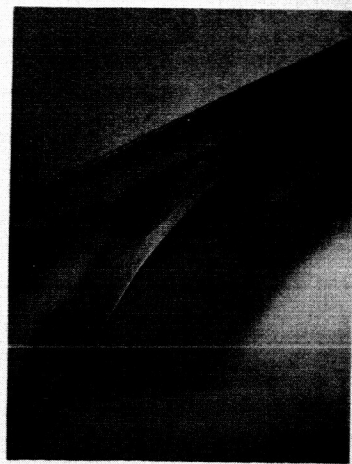
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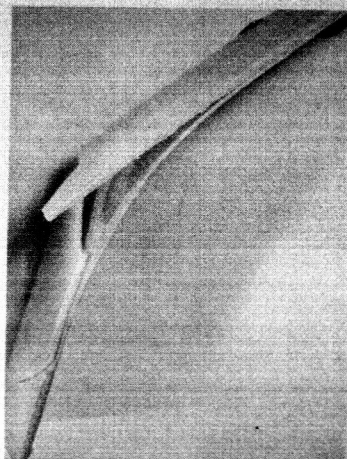
Formulation 46



Formulation 47



Formulation 48



Formulation 49



Formulation 50



Formulation 51

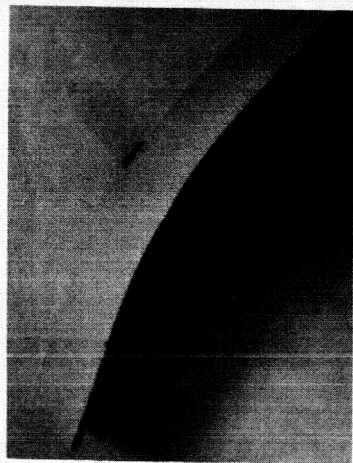


Formulation 52

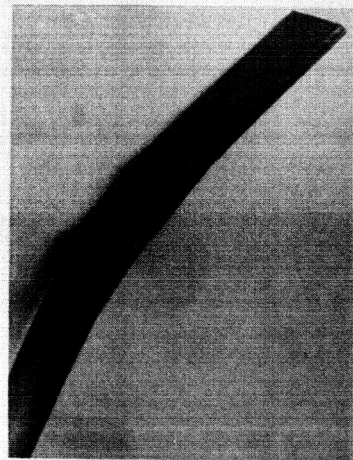


Formulation 53

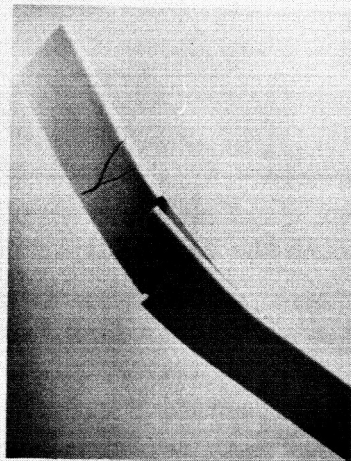
FIGURE 4A (cont'd)



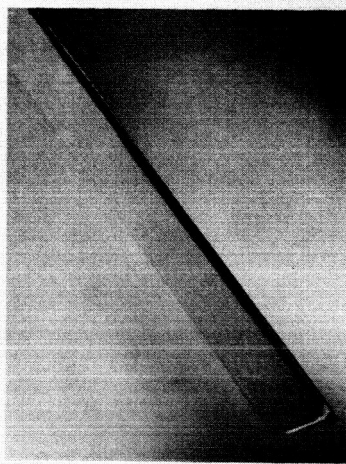
Formulation 54



Formulation 55



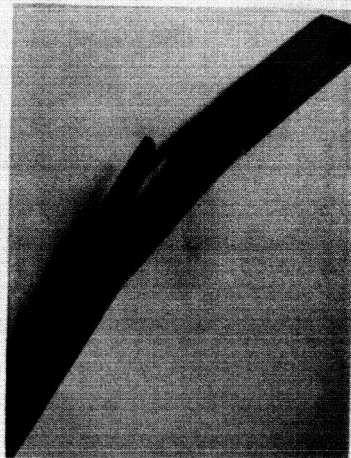
Formulation 56



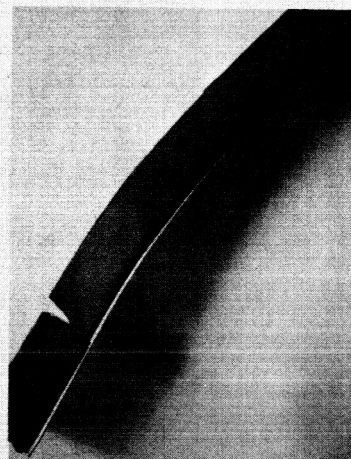
Formulation 57



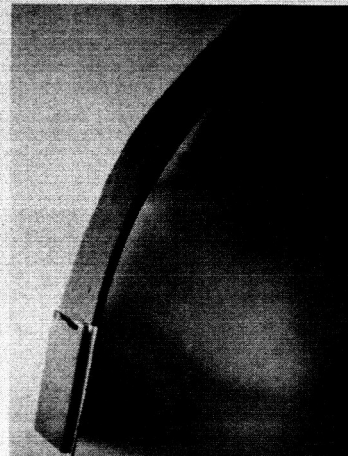
Formulation 58



Formulation 59



Formulation 60



Formulation 61



Formulation 62

## THERMAL CONTRACTION STUDIES

It must be realized that the low temperature flexibility test, although designed to separate candidate materials and rank them according to their low temperature utility, is quite severe. Other tests must also be used to select the best possible material and a study of the contraction properties of the sealants and base polymers is also necessary. Volume changes at transition temperatures must be held to a minimum and the coefficients of thermal contraction should match, as closely as possible, the metal substrates.

Cylindrical specimens, approximately 3 inches long and 1/2 inch in diameter, were placed in a quartz tube suspended in a Dewar flask. A thin quartz rod, resting on the specimens, protruded above the tube. A cathetometer was used to measure the change in height of the rod and thus the contraction of the specimens. N-propanol was used as the bath and was cooled by the addition of liquid nitrogen. After each addition, the temperature was measured with a copper-constantin thermocouple imbedded in the specimen and the length measurements were made after the specimen temperature had stabilized for 15 minutes. The bath was only useful to approximately 170°K, thus near this temperature the tests were interrupted and liquid nitrogen was substituted for the bath and the final point was taken at 80°K. For comparison, the contraction was measured in a direct run by rapid cooling to 80°K. The apparatus in operation is shown in Figure 5.

Specimens of EC 1667 and Adiprene L-100 formulations were tested initially. Their contraction characteristics are shown in Figure 6 and 7. The relatively large volume change, at the crystallization temperature, of EC 1667 is shown at about 210 to 220°K and is typical of crystallizable silicone elastomers<sup>(37)</sup>. Very little crystallization, at the cooling rate used, was observed for the Adiprene.

Curves were then plotted for the Adiprene L-100 and castor oil, representing a straight polymer, and the same formulation filled with milled glass fibers. The effect of the filler was to duplicate the





FIGURE 5 THERMAL CONTRACTION APPARATUS

# RATE OF THERMAL CONTRACTION

EC 1667

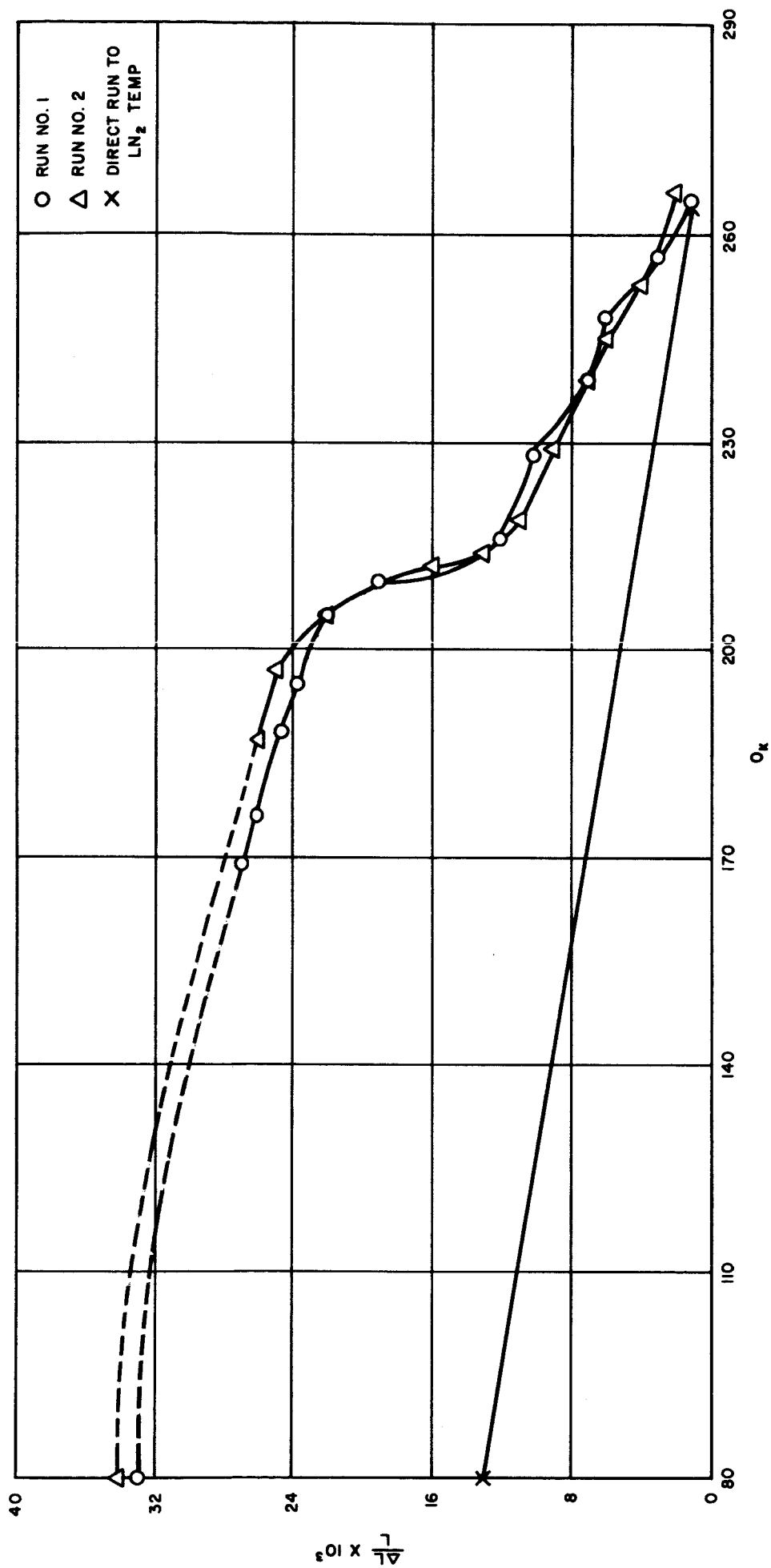


FIGURE 6

# RATE OF THERMAL CONTRACTION ADIPRENE, MOCA, FLEXOL TOF

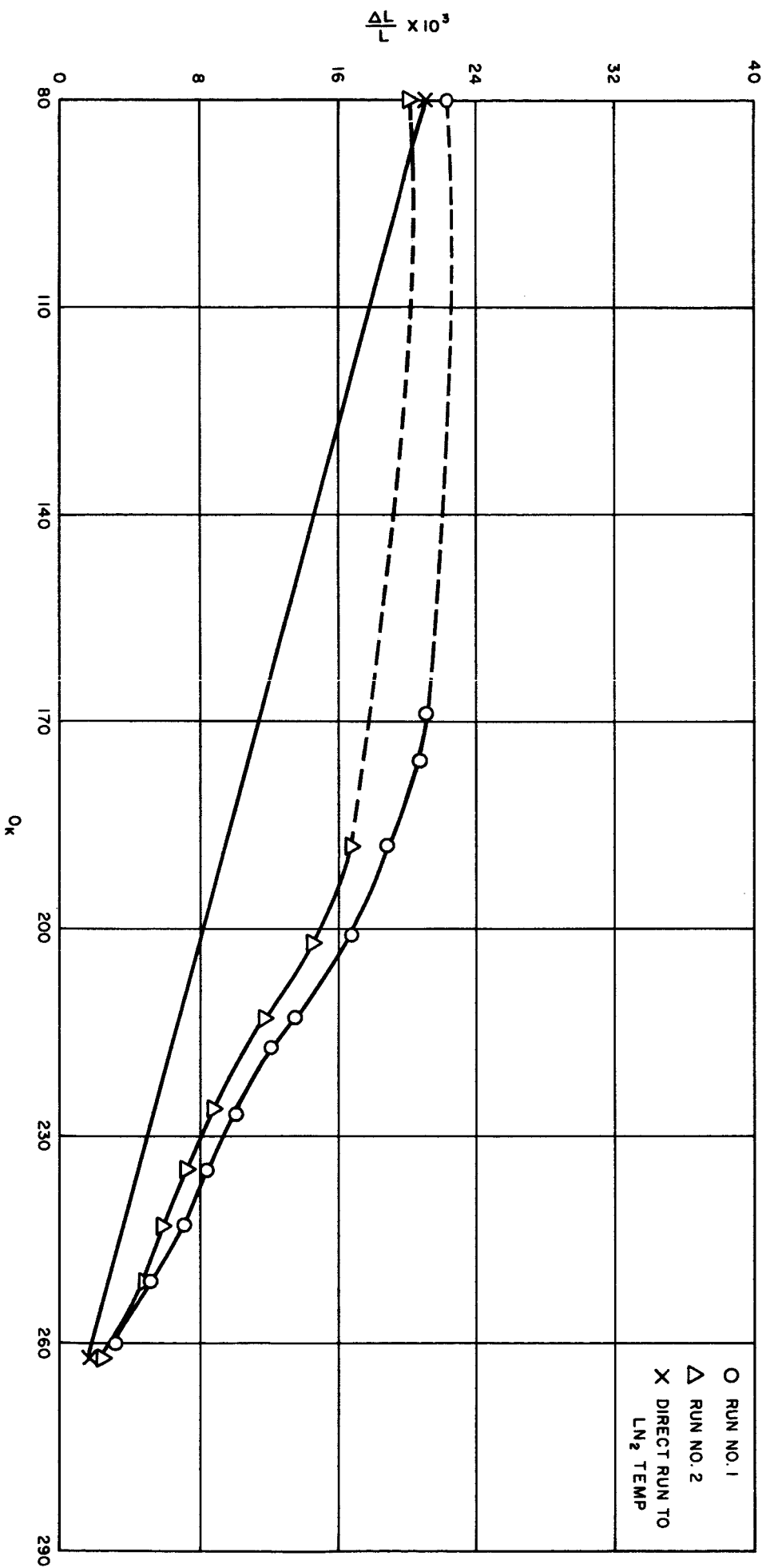


FIGURE 7

reduction in the over-all coefficient of thermal contraction due to the glass fabric. These curves are shown in Figures 8 and 9.

Ideally, for the sealant to meet the requirements of use down to 20°K, it would have its glass transition temperature below 20°K. This has not been attained by any known organic material. In fact, polyethylene, having the lowest glass transition temperature of the known polymers, reaches its glassy state well above 76°K. One must be more realistically concerned with a polymer's flexibility and toughness in the glassy state. As an example, the crystalline nature and brittleness of polyethylene makes it less suitable as a cryogenic sealant than the materials under investigation in this program. The development of sealants with the lowest glass transition temperatures is not the primary objective because of another effect. For pure polymers, low glass transition temperatures and a small difference between the thermal expansion (or contraction) coefficients are mutually incompatible. This follows from a result of Simha and Boyer<sup>(38)</sup> showing that for linear amorphous polymers, the product of the glass transition temperature and the coefficient differences is a constant. By lowering the glass transition temperature of a pure polymer one expects to increase the difference between its coefficient of thermal expansion above and below its glass transition temperature, thereby obtaining a larger volume change at this temperature.

$$(\alpha_r - \alpha_g) T_g \approx 0.113$$

where

$\alpha_r$  = coefficient of the thermal expansion above the glass transition temperature

$\alpha_g$  = coefficient of thermal expansion below the glass transition temperature

$T_g$  = glass transition temperature.

FIGURE 8  
RATE OF THERMAL CONTRACTION  
ADIPRENE, CASTOR OIL

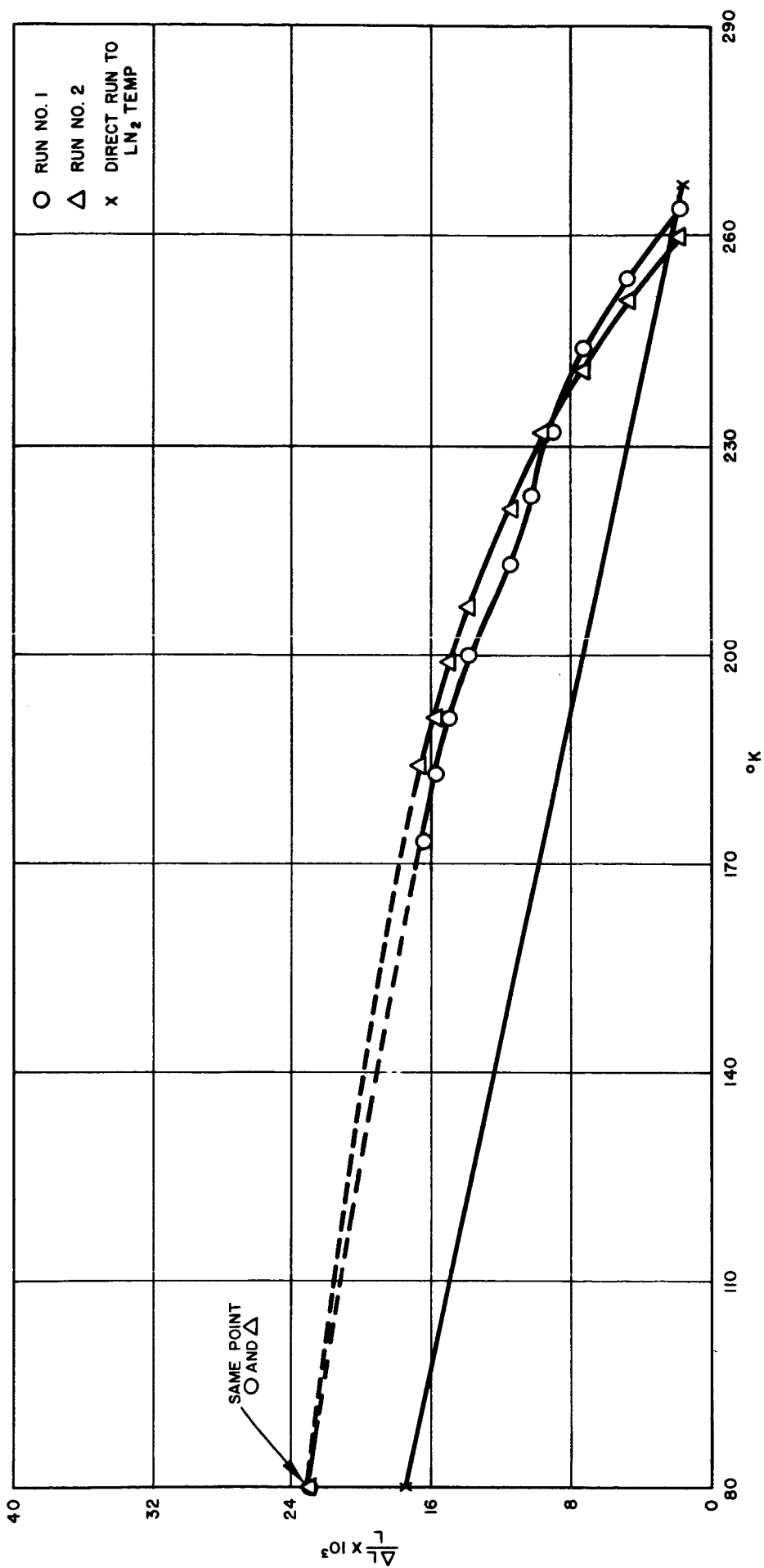
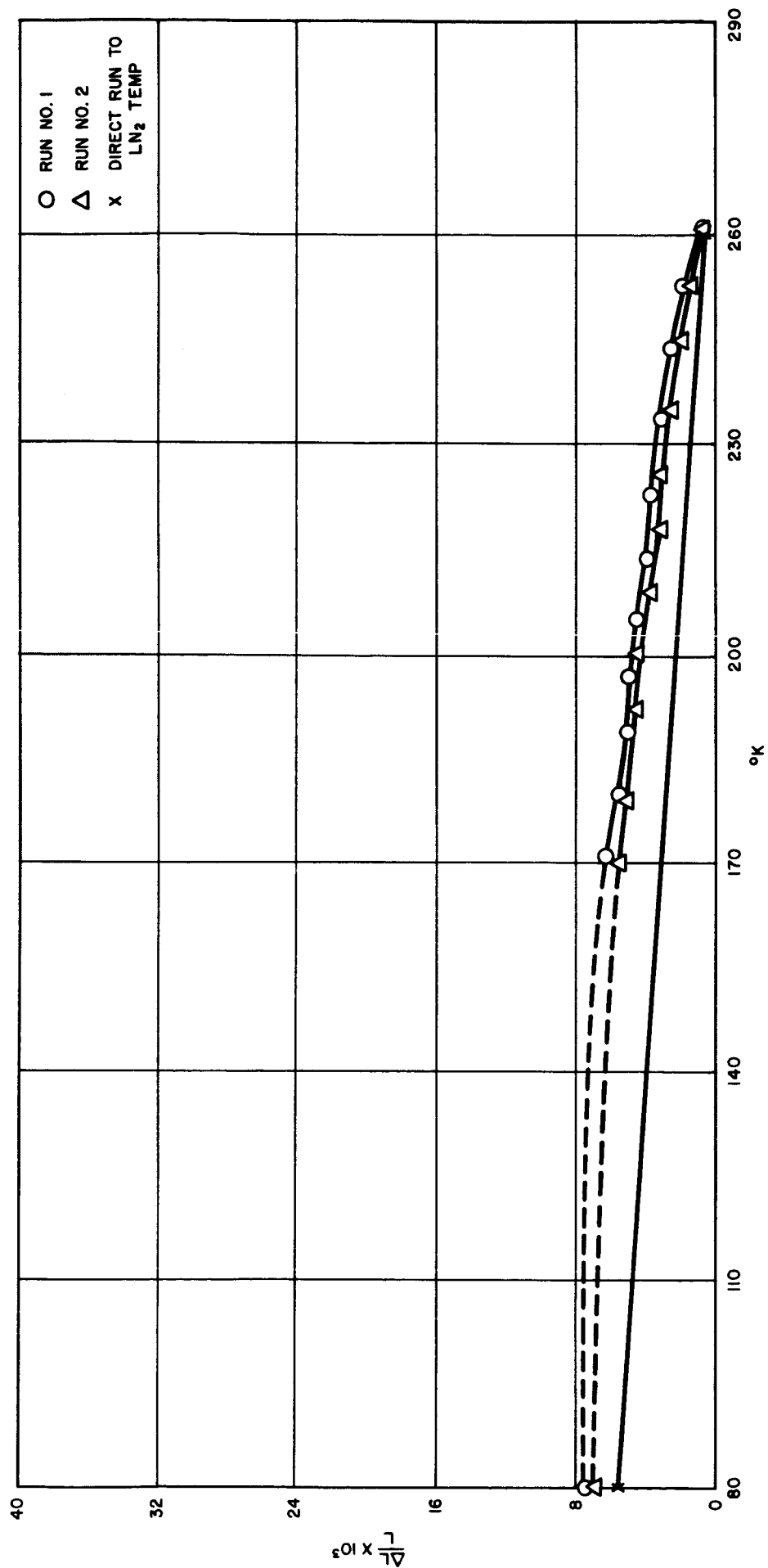




FIGURE 9  
 RATE OF THERMAL CONTRACTION  
 ADIPRENE, CASTOR OIL, MILLED GLASS FIBERS



However, when a filler is used in a pure polymer, this relationship changes. Note that in Figure 8 and 9 a lower over-all slope was obtained, with the glass fiber filler, and any changes in slope were reduced. Using a 40 percent by weight loading of E-glass fibers in the Adiprene polymer gave an over-all coefficient of thermal expansion (contraction) of  $29 \times 10^{-6}$  in/in/°C, approximating that of aluminum.

#### Discussion of Effects of Loading Upon the Coefficient of Thermal Expansion of Elastomeric Compounds

Two important features of the cryogenic organic sealant problem are adhesive strength and thermal expansion behavior of the sealant. With two diverse materials such as an organic elastomer and a metal, ordinarily the thermal expansions are considerably different and thus temperature changes can result in the development of high thermal stresses in the elastomer. Thus the elastomer must possess a high ultimate strength in order to withstand rupture under these stresses. However the situation contains the elements of a "trade-off" in that if the coefficient of thermal expansion of the sealant can be closely matched to that of the metal, a sealant of lower strength could be used. These considerations led to the investigation of formulating elastomers with fillers.

It was thought that the development of approximate relationships between the properties of the ingredients to be used and the properties of the compounds might aid in this phase of the work. That is, if predictions could be made with satisfactory accuracy, then it might be possible to eliminate certain combinations from consideration and, in other cases, to reduce the number of formulations to be compounded with other combinations. However in addition to reducing the total amount of work to be performed, there existed the possibility that the relationships might be of value in interpreting experimental results.

#### Loading With Finely-Divided Filler

It was decided first to consider the simplest case, viz. that of small particles of filler embedded in a matrix of elastomer.

The first assumption made is that the coefficients of thermal expansion of the ingredients are constants independent of temperature. Although this applies in the case of fillers, it is not true of elastomers. In the latter case we have one constant below, and another above, the glass transition temperature. However this does not constitute a serious objection because measurements made in the laboratory straddle the glass transition temperature by a wide range. Thus the calculated coefficient represents an "average" over this range and can be used as long as all measurements are made consistently in this way. (This was the case for the work reported in this section.)

The second assumption is that the total volume of material is equal to the sum of the filler volume and the elastomer volume. This is equivalent to assuming that none of the filler dissolves in the elastomer and that the surface of each filler particle is completely "wetted" by the elastomer (no air or gas film on the surface).

The third assumption is that both the elastomer and the filler are incompressible. Although this is true of all elastomers (Poisson's ratio being very close to 0.5), it is not true of fillers in general. However since the filler volume changes due to thermal stresses at the surface would probably be small, it was decided to accept this assumption in the interests of simplicity. Comparisons of observed and calculated values could be used later to establish the seriousness of the discrepancy due to making this assumption.

Let

$\alpha_i$  = coefficient of material  $i$

$\alpha_m$  = coefficient of the mixture

$V_i$  = initial volume fraction of material  $i$

Initially

$$V_1 + V_2 = 1 \quad (1)$$

After a one degree temperature rise

$$(1 + \alpha_m)^3 = V_1 (1 + \alpha_1)^3 + V_2 (1 + \alpha_2)^3 \quad (2)$$

from (1) and (2) we obtain the approximation

$$\alpha_m = V_1 \alpha_1 + V_2 \alpha_2 \quad (3)$$

It was decided to check this relationship by comparing calculated values with observed values obtained on filled epoxy formulations. <sup>(39)</sup>

Calculations were made for all formulations where data on the properties of the ingredients were available. The results are shown in Table III along with the observed values. (Each value shown for a given filler-resin combination represents a different volume loading.)

If the relationship were correct, one would expect the discrepancies between the observed and calculated values to be due to errors of measurement (weights, lengths, and temperatures). It would also be logical to expect positive errors to occur as frequently as negative errors. However inspection of the table reveals that high calculated values occur more frequently than low ones. The actual distribution is

<u>Type of Error</u>	<u>Number of Values</u>
Calculated value too high	13
Calculated value correct	4
Calculated value too low	4

It was decided to check the significance of the distribution for the hypothesis that highs and lows should have been equal in number.

A chi-squared test showed that the above distribution of highs and lows was significant at a level,  $.02 < P < .05$ . Thus the relationship has a bias such that calculated values tend to be too high.

	Coefficients x 10 <sup>6</sup>	
	Observed	Calculated
Silica	26	25
Silica	45	45
Silica	46	46
Aluminum (MD-101)	34	39
Aluminum (MD-101)	44	44
Aluminum (MD-101)	48	48
Stupalith 2410	19	18
(Lithium Aluminum Silicate)	33	36
(Lithium Aluminum Silicate)	47	44
Calcium Carbonate	23	28
Calcium Carbonate	46	44
Iron Powder (MD 180)	33	38
Iron Powder (MD 180)	45	48
Copper Powder (MD 151)	36	42
Copper Powder (MD 151)	47	49
Hydrated Alumina C-730	41	45
Hydrated Alumina C-730	46	48
Aluminum Oxide fines	30	39
Aluminum Oxide fines	41	45
Alumina A-2 (325 mesh)	30	38
Alumina A-2 (325 mesh)	41	45

Table III. Coefficients of thermal expansion of filled Epon 828.

It is possible that the bias is due to use of Assumption No. 3. However since the discrepancies are rather low in magnitude, it was decided to accept the equation as a rough working tool.

Following the above, calculations were made to determine the feasibility of matching the coefficients of aluminum and steel with Adiprene loaded with lithium aluminum silicate. (The latter is a filler with a negative coefficient of thermal expansion.)

The following data were used to calculate the formulations.

<u>Material</u>	<u><math>\alpha</math> (deg. C)<sup>-1</sup></u>
Adiprene-castor oil	+84 x 10 <sup>-6</sup>
Aluminum	+25.5
Steel	+10.0
Lithium aluminum silicate	- 6.0

The calculated filler volume fraction was 0.65 for aluminum and 0.82 for steel. If we assume (a) the filler particles to be very small uniform spheres and (b) the closest packing ratio (0.74), then obviously an aluminum match is attainable but not a steel match.

Assuming the closest packing ratio, the lowest obtainable coefficient for this combination of ingredients is  $17 \times 10^{-6}$ /deg.C.

#### Loading With Fibers

It was desired to estimate the coefficient of thermal expansion of a mixture consisting of a mass of fibers embedded in a matrix of elastomer.

In order to simplify the derivation of a relationship in terms of the coefficients and quantities of the two materials, in addition to the assumptions used above, the following assumptions were made:

1. Each fiber is a rigid rod of infinite length/radius ratio.  
This assumption permits one to neglect "end effects."
2. The elastomeric material about a fiber can shrink freely in the radial direction of the rod (fiber) in accordance with its coefficient of thermal expansion.

3. The elastomer is constrained in shrinkage axially to that of the glass fiber.

Based on the above assumptions one can consider measurements made under two extreme conditions. If all of the fibers were oriented with their axes parallel to one another and to the direction of measurement, then the measured coefficient of thermal expansion would be equal to that of the fiber material. However if all of the fibers were oriented with their axes perpendicular to the direction of measurement, then the measured coefficient would be the volume-weighted mean of the coefficients of the two materials (as shown previously for finely divided fillers). In the normally expected situation neither of the above would apply and instead one would encounter the random or hay-stack type of orientation of axes to direction of measurement. But this random orientation implies that every possibility between the above extremes would exist. If it is assumed that every possibility is equally probable, then each of the extremes can be assigned an equal weight.

(Alternatively, we can consider the rods as vectors. Each vector can be decomposed into two components; one a vector in a plane perpendicular to the direction of measurement and the other component a vector parallel to the direction of measurement. Thus the original volume of material can be considered as equivalent to two half-volumes in series with respect to direction of measurement. One half-volume contains only parallel vectors and the other half contains an equal number of perpendicular vectors.)

The above can be expressed symbolically as

$$a_m = .5a_P + .5a_N \quad (4)$$

where

$a_m$  = coefficient of the mixture

$a_P$  = coefficient for parallel orientation of axes to measurement direction

$a_N$  = perpendicular orientation coefficient

But

$$a_P = a_g \text{ and } a_N = V_g a_g + V_e a_e$$

where

g applies to glass (fiber)

and

e applies to elastomer

and

V is volume fraction

With these relationships and (4) we get

$$a_m = \frac{(1 + V_g) a_g + V_e a_e}{2} \quad (5)$$

It was decided to use this relationship to calculate a coefficient for comparison with one actually measured in the laboratory.

The material was a mixture of E-glass fibers embedded in a matrix of Adiprene cured with castor oil. The data on the ingredients of the mixture were:

	<u>Adiprene Castor Oil</u>	<u>E-glass</u>
Weight - %	60	40
$\alpha (\text{deg. C})^{-1} \times 10^6$	84	5
Density - g/cc.	1.06	2.58
Volume %	78.5	21.5

The measured "average" coefficient over the approximate range of 265K to 80K of the mixture was  $29 \times 10^{-6}$ .

The coefficient calculated from the above data and Equation (5) was  $36 \times 10^{-6}$ . Thus the calculation provides only a rough approximation to the correct value. It should be observed that the discrepancy is



in the same direction as those previously discussed in the case of the finely divided fillers. Thus the same comments would apply here but, in addition, consideration should be given to the possibility that the use of Assumption No. 1 may also be responsible for part of the discrepancy.

However it should be pointed out that the use of Equation (5) as a "shape factor" equation has some merit. To illustrate: a calculation based on the relationship for finely divided fillers and the same data as above yields a value of  $67 \times 10^{-6}$ . Thus the discrepancy between calculated and observed value is considerably greater than that obtained by use of Equation (5).

The above is of interest in that it implies that, in work directed toward tailoring coefficients of materials, the geometry of the filler should be given equal consideration with its quantity.

Calculations made in the case of finely divided fillers indicated that with lithium aluminum silicate and Adiprene the coefficient of steel could not be matched because the required filler volume fraction would exceed that of the closest packing ratio. It was thought that it would be of interest to calculate the required volume fraction on the assumption that the filler was available in the form of fibers.

It was found that under these conditions the coefficient of steel could be matched with Adiprene loaded with 0.64 volume fraction of lithium aluminum silicate. (The closest packing volume fraction for rigid rods is 0.90.) Thus there is a possibility of a match in this case. However, due to the strengthening effect of fibers, an exact match is not necessary.

## SYNTHESIS OF NEW POLYMERS

The following criteria of molecular structure are considered necessary to achieve flexibility in elastomers below their glass transition temperatures:

1. short statistical segmental length
2. high segmental mobility
3. small, non-polar substituents on the polymer chain
4. high rotational freedom about the polymer chain bonds

It is recognized that these criteria are redundant in most cases. However, the structure of linear polysiloxanes most closely meet these requirements

Short statistical segmental lengths can be obtained by a low crosslinking density; this is most easily done by copolymerizing a cyclic dimethylsiloxane with a small mole percent of cyclic methylvinyl siloxane. Appropriate quantities of a reactive filler may be used to compromise the sacrifice in mechanical strengths brought about by low vinyl content.

High segmental mobility is inherent in the siloxane backbone. Further mobility would result from a reduction in symmetry about the polymer chain. Inclusion of 2-6 mole percent of methylphenyl groups in a polydimethylsiloxane has proven to be a satisfactory method for improving low temperature flexibility. Momentarily neglecting the inherent chemical instability of optional side groups it would appear feasible to copolymerize small quantities of chloromethyl methyl cyclic siloxanes or methyl cyclic siloxanes with the cyclic dimethylsiloxane. There is evidence that such polymers would have improved low temperature characteristics. <sup>(40)(41)</sup> The volume of these suggested groups would be considerably less than phenyl, trifluoropropyl or cyanoethyl groups, all of which are presently available.

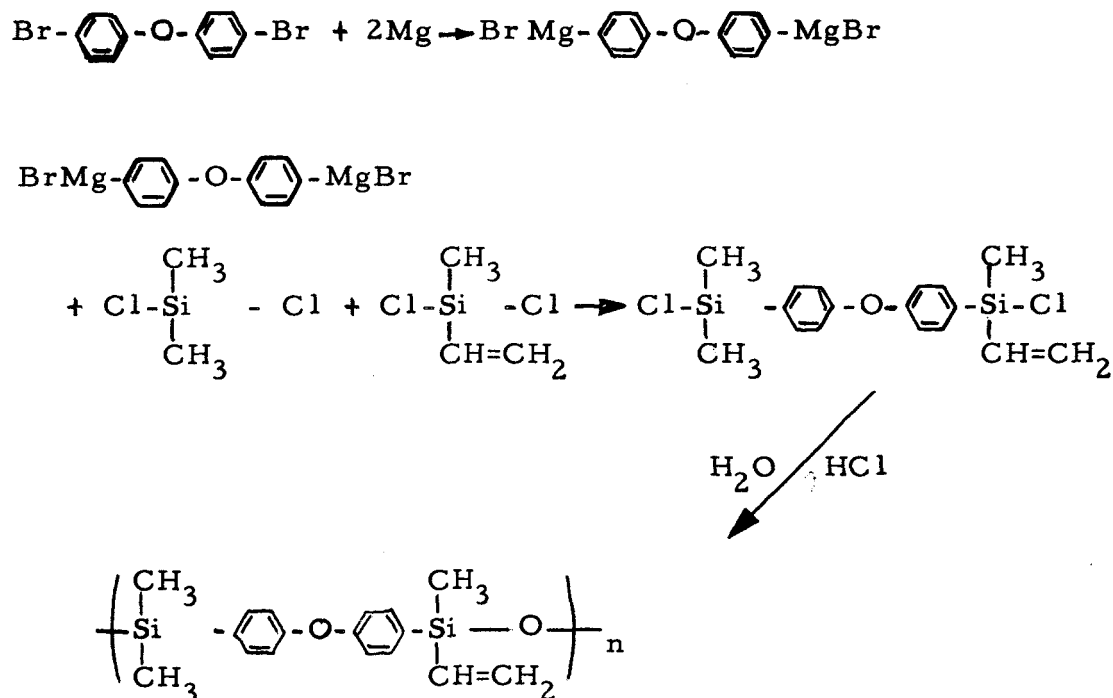
The polarity of the side groups, which, in the case of polysiloxanes, affects both the hydrolytic stability and interchain associations (the latter leading to increased crystallinity) need not be a limiting factor if the number of such groups is small and if these groups are

suitably protected by chain entanglement. Hydrolytic instability of silicon oxyhydride for example is good since the polymer is sufficiently insoluble to prevent such interaction. Instability in acids or bases is still another question and depends upon the environment in which the elastomer must operate.

High rotational freedom about the polymer chain bonds is also inherent in the polysiloxane molecule and is similarly effected by the nature of the polymer side groups.

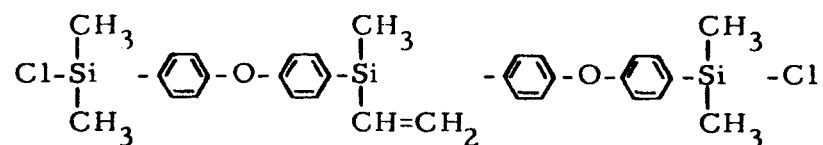
Based upon the above observations, and consideration of other proposed polymeric structures, the initial effort was placed on the modified polysiloxanes.

A poly (phenyl ether silicone) elastomer (B2351-13) was prepared as follows:



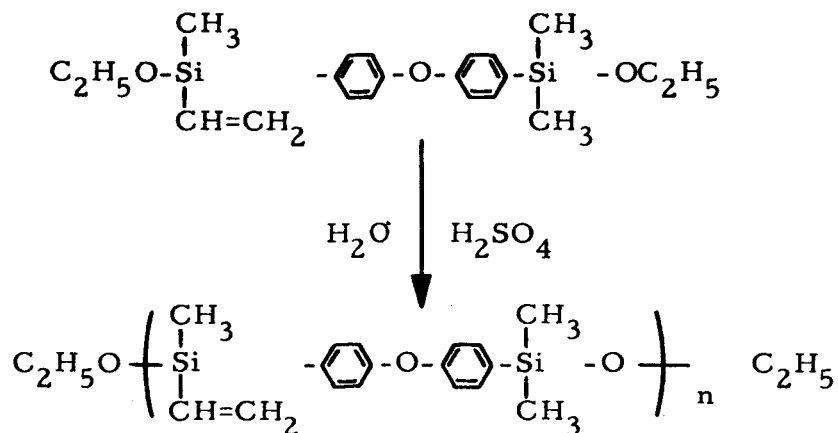
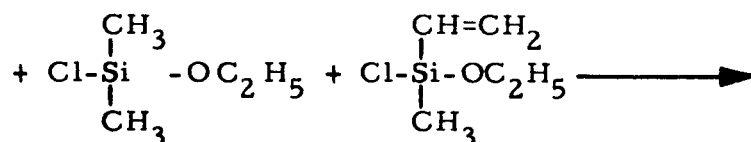
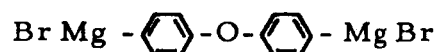
Bis (4-bromophenyl) ether was converted to its di-Grignard reagent, which was condensed with an equimolar mixture of dimethyldichlorosilane and methylvinylchlorosilane. The resultant monomer

was hydrolyzed with hydrochloric acid to the silicone elastomer. Unfortunately, the reaction of the di-Grignard reagent with the dichlorosilanes can result in further condensation to compounds such as



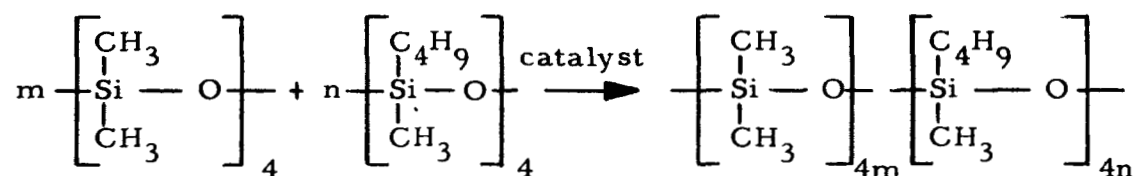
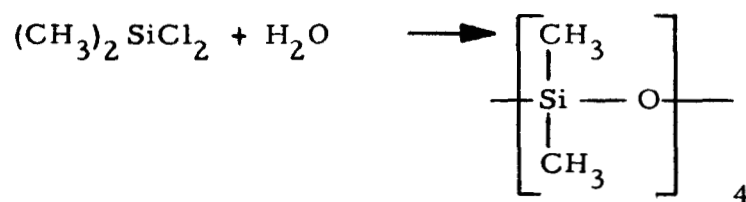
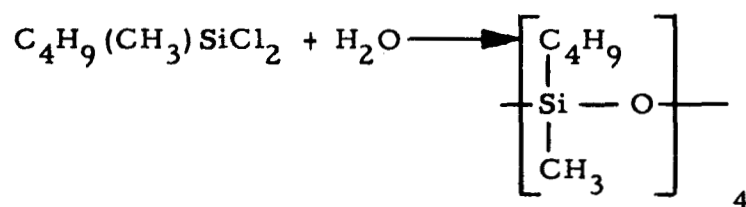
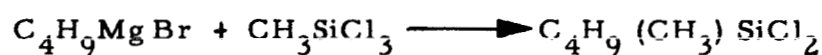
The silicone polymer formed by hydrolysis of this compound would tend to be somewhat more rigid and less rubbery than the polymer without

$-\text{C}_6\text{H}_4-\text{Si}-\text{C}_6\text{H}_4-$  groups. Hence a similar polymer (B2351-14) was prepared by condensing the di-Grignard reagent with chloroethoxysilanes.



Bis (4-bromophenyl) ether was again converted to the di-Grignard reagent, which was then condensed with a mixture of dimethylchloroethoxysilane and methylvinylchloroethoxysilane (approximately 2:1 ratio). The resultant monomer was hydrolyzed with sulfuric acid. Further hydrolysis of part of the product resulted in an increase in the molecular weight of the polymer.

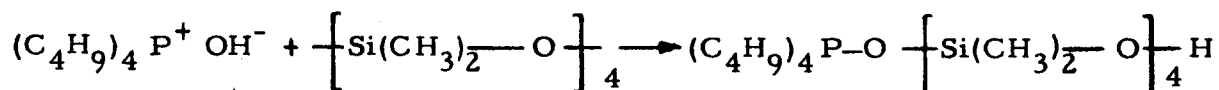
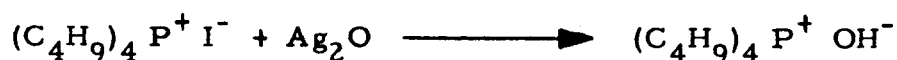
Several polybutylmethyilsiloxanes, containing 0, 5, and 10 percent butyl groups, have been synthesized according to the following equations:



n-Butyl bromide was converted to the Grignard reagent, which reacted with methyltrichlorosilane to form butylmethyldichlorosilane. This was hydrolyzed to a mixture of cyclic butylmethyilsiloxanes (mostly the tetramer). Similarly dimethyldichlorosilane was hydrolyzed to

dimethylsiloxane tetramer. The two tetrameric siloxanes were mixed in definite proportions and copolymerized by heating in the presence of a catalyst to high-molecular-weight linear polysiloxanes.

The catalyst was made from tributylphosphine as follows:



The tributylphosphine was treated with butyl iodide, and the resulting quaternary iodide was converted by an aqueous silver oxide suspension to the quaternary base. This base was dissolved in tetrameric dimethylsiloxane and the water removed by distillation. The tetrabutylphosphonium silanolate thus synthesized is a good polymerization catalyst for the preparation of polysiloxanes, and also can be decomposed after the polymerization is completed to prevent depolymerization from taking place.

A rubber was prepared from a sample of a linear polysiloxane using benzoyl peroxide as the catalyst and a silica filler. After being blended on a rubber mill, it was cured, in an oven, for 3 hours at 95°C.

Bend test specimens were prepared; however good adhesion to the aluminum substrate was not attained. Future work will involve a study of curing mechanisms and methods to increase the adhesion to aluminum. In addition, these rubbers, both filled and unfilled, will be studied to determine their thermal contraction characteristics. Thus the degree of volume change will be measured and an estimate of the degree of crystallization will be estimated.

## Experimental

### Polymer B2351-13

A solution of bis (4-bromophenyl) ether (109 gm., 0.3 mole) in tetrahydrofuran (220 cc.) was carefully added to a slurry of magnesium (17 gm.) in tetrahydrofuran. After the addition was complete (3/4 hr.) the mixture was heated at reflux for four hours. A solution of dimethyldichlorosilane (19 gm., 0.15 mole) and methylvinylchlorosilane (21 gm., 0.15 mole) was then added over a 20 minute period and reflux was maintained for 3/4 hr. Additional tetrahydrofuran (1.5 l.) was then added and after six hours under reflux the mixture was poured over ice and concentrated hydrochloric acid (25 cc.). After stirring overnight, the product was thoroughly washed with water and dried over sodium sulfate. Evaporation of the solvent under vacuum (at 70°C) yielded a solid product (44 gm., m.p. approx. 80°C.).

### Polymer B2351-14

Bis (4-bromophenyl) ether (109 gm., 0.3 mole) was dissolved in tetrahydrofuran (320 cc.) and the solution was then slowly added to a mixture of magnesium (16 gm., 0.66 mole) in tetrahydrofuran (75 cc.). The addition required one hour and after completion the slurry was heated at reflux for three hours. Additional tetrahydrofuran (50 cc.) and a mixture of dimethylchloroethoxysilane (54 gm., 0.39 mole, B.P. 95°C) and methylvinylchloroethoxysilane (32 gm., 0.21 mole, B.P. 116°C) were added over a 15 minute period. After refluxing for 3-1/4 hr., the mixture was poured over ice and concentrated sulfuric acid (20 cc.) was carefully stirred in. After stirring overnight at ambient temperature the organic phase (400 cc.) was divided into 2 portions.

The first portion (A) was washed four times with water (500 cc.) and the solvent was removed by vacuum distillation giving a thick syrupy polymer (42 gm., 49% yield).

The second portion (B) was chilled to 0°C and additional sulfuric acid (150 cc.) was added and, after stirring for 1-1/2 hours, the mixture was allowed to warm to ambient and was stirred two additional

hours. After carefully washing five times with water and drying with  $\text{Na}_2\text{SO}_4$  and  $\text{CaCl}_2$ , the solvent was removed under vacuum. This fraction of polymer weighed 37 grams (48% yield) and was quite rubbery, indicating a significantly higher molecular weight material.

#### n-Butylmethyldichlorosilane (B4018-44)

n-Butylmagnesium bromide solution was prepared by the addition during six hours, of 1370 g. of n-butyl bromide to 243 g. of magnesium turnings in 5 l. of anhydrous ethyl ether. After refluxing for two hours, the resulting Grignard solution was added to 1495 g. of distilled methyltrichlorosilane in 1.5 l. of anhydrous ethyl ether and the mixture was refluxed for several hours. A large part of the ethyl ether was distilled. Then 1500 g. of dry decalin was added and material distilling up to about  $176^\circ\text{C}$  was collected. The distillate was redistilled twice through a Vigreux column, yielding 707 g. (41%) of product distilling at  $150\text{--}156^\circ$ .

#### 1, 3, 5, 7-Tetrabutyl-1,3,5,7-tetramethylcyclotetrasiloxane (B4018-48)

To 1770 ml of water maintained at  $15\text{--}20^\circ\text{C}$  was added, with stirring, 707 g. of n-butylmethyldichlorosilane during 4-3/4 hours. The aqueous phase was extracted twice with ethyl ether. The ether extracts were combined with the organic phase and dried over anhydrous potassium carbonate. After distillation of the ether at atmospheric pressure, the residue was distilled at 17 mm pressure. The distillate was redistilled at the same pressure, and the fraction boiling at  $158\text{ to }195^\circ\text{C}$  at 17 mm was collected (197 g., 41% yield). This distillate is a mixture of various butylmethyl cyclosiloxanes, probably from the cyclotrisiloxane through the cyclohexasiloxane.

#### Octamethylcyclotetrasiloxane (B4018-26)

To 3 liters of  $\text{H}_2\text{O}$  maintained at  $15\text{--}20^\circ\text{C}$  in a 5-l. three-neck flask was added, with stirring, 1200 ml. (1272 g.) of dimethyldichlorosilane (technical grade) during 3 hours. The aqueous phase was then



extracted twice with ethyl ether, and the ether extract was added to the organic phase. After drying over anhydrous potassium carbonate, the mixture was distilled through a Vigreux column at atmospheric pressure. The fraction distilling at 160 to 175°C was redistilled through the Vigreux column. The product boiled at 167-168°C (uncorrected) and weighed 342 g. An attempt was made to convert the higher molecular weight siloxanes into tetramer by heating in a metal bath at 400°C for several hours, but it was unsuccessful.

#### Tetra-n-butylphosphonium Iodide (B4018-2)

Tri-n-butylphosphine (3.5 g.) in 50 ml. of ethanol was treated with 3.2 g. n-butyl iodide in 50 ml. of ethanol under a nitrogen atmosphere. After short heating the product (3.2 g.) was precipitated by the addition of cyclohexane. It was recrystallized twice from benzene-cyclohexane.

#### Tetra-n-butylphosphonium Hydroxide (B4018-36)

A solution of 6.8 g. of silver nitrate in 40 ml. of water was added with stirring to a mixture of 6.3 g. of barium hydroxide octahydrate in 100 ml. of hot water. After cooling the mixture was centrifuged and the silver oxide precipitate was washed by decantation. The precipitate, suspended in 20 ml. of water, was treated with 7.7 g. of tetra-n-butylphosphonium iodide and stirred overnight. After filtering, the filtrate was concentrated in vacuum at room temperature to about 15 ml.

#### Tetra-n-butylphosphonium Silanolate (B4018-37)

The aqueous solution of tetra-n-butylphosphonium hydroxide (15 ml.) was added to 200 ml. of octamethylcyclotetrasiloxane. The mixture was distilled at room temperature under vacuum until only one liquid phase remained. On standing, the solution became more viscous, indicating that some polymerization of the solvent was taking place even at room temperature.

### Preliminary Polymerizations of Cyclosiloxanes (B4018-41)

Three polymethylbutylsiloxanes were prepared, with the following compositions:

- A. 100% methyl groups;
- B. 5% n-butyl groups, 95% methyl groups;
- D. 10% n-butyl groups, 90% methyl groups.

For this purpose, three solutions were prepared from octamethylcyclotetrasiloxane (I) and tetrabutyltetramethylcyclotetrasiloxane (II):

- A. 30 ml. of I
- B. 3 ml. of II plus 27 ml. of I
- C. 6 ml. of II plus 24 ml. of I

These solutions were then heated to 110°C in an oil bath under nitrogen and treated with 2 ml. of tetrabutylphosphonium silanolate catalyst solution. Solution A became stiff within five minutes, and was removed from the heating bath after one hour. Solutions B and C thickened and yellowed, but did not become stiff, so they were heated for 18 hours. After cooling, solution B was stiff but solution C still flowed slowly. The three solutions were then heated at 190 - 200°C for three hours to decompose the polymerization catalyst.

## VIBRATION TESTING AT LIQUID NITROGEN TEMPERATURE

In use, the sealants will be exposed to shock and vibration loads of various frequencies and amplitudes. A test fixture was designed and a procedure was developed to determine if vibrations of various intensities, through a schedule of conditions, specified by the sponsor, would cause failure in a sealed joint. It is here used as an evaluation technique on candidate sealants found through previous screening tests to be the best available. Adiprene L-100, cured with castor oil and reinforced with 6 plies of 181 style glass fabric, was tested and at 76°K withstood all vibration loads to which it was subjected.

The fixture consists of a hollow aluminum block with a removable plate forming one wall. The specimen is bonded to this wall with the sealant, and liquid nitrogen is poured into the hollow chamber to cool the entire fixture and specimen. The sealant thickness is arbitrarily kept at a nominal 1/16 inch. A thermocouple embedded in the sealant measures the temperature and monitors the flow of liquid nitrogen. The specimens used in the tests conducted during the report period were 0.032 x 1 x 6 inch. aluminum strips with a 1/8 inch radius bend to give a free horizontal arm for loading and to which an accelerometer is mechanically attached. The wall plate to which the sealant is bonded is removable to allow new specimens to be inserted easily in the mounted fixture. The fixture assembly before testing is shown in Figure 10.

The reinforced Adiprene L-100 sealant was subjected to the five vibration categories, at 76°K, specified by the sponsor, starting with the easiest category 5 and working backwards to the most severe category 1. The frequencies were scanned through the range of 20-2000 cps and resonance frequencies were held for either 5 or 10 minute intervals. The conditions are summarized in the following table. Note that for category 2 an intermediate range resonance frequency was used because 50 g loads at frequencies in the 1470 range would have been beyond the equipment capabilities. Likewise, only the low resonance frequency was used in category 1. The 41 - 43 cps

Category	Resonance Frequencies	Loads at Resonance Frequencies
5	43 cps (10 Min.)	2 g's
	1472 cps (10 Min.)	10 g's
4	43 cps (10 Min.)	6 g's
	1472 cps (10 Min.)	25 g's
3	1447 cps ( 5 Min.)	35 g's
2	40 cps ( 5 Min.)	8 g's
	516 cps ( 5 Min.)	50 g's
1	41 cps ( 5 Min.)	10 g's

frequencies, especially in the high g range of categories 1 and 2, were extremely severe, causing the largest movement in the free arm. The fixture and specimen during the test are shown in Figure 11.

When the test was concluded and the accelerometer was being removed, the aluminum specimen broke at the bend. The sealed joint was still intact, however, with the shorter specimen segment still attached to the plate. This metal fatigue failure must have occurred at the end of the last 5 minute run. It did not occur before this, because the previous scanning traces made from the accelerometer input did not show any abnormalities.

In the future, test specimens will be made from slightly heavier gauge metals and with a larger radius bend. Thus, fatigue failure of the metal may not be encountered.

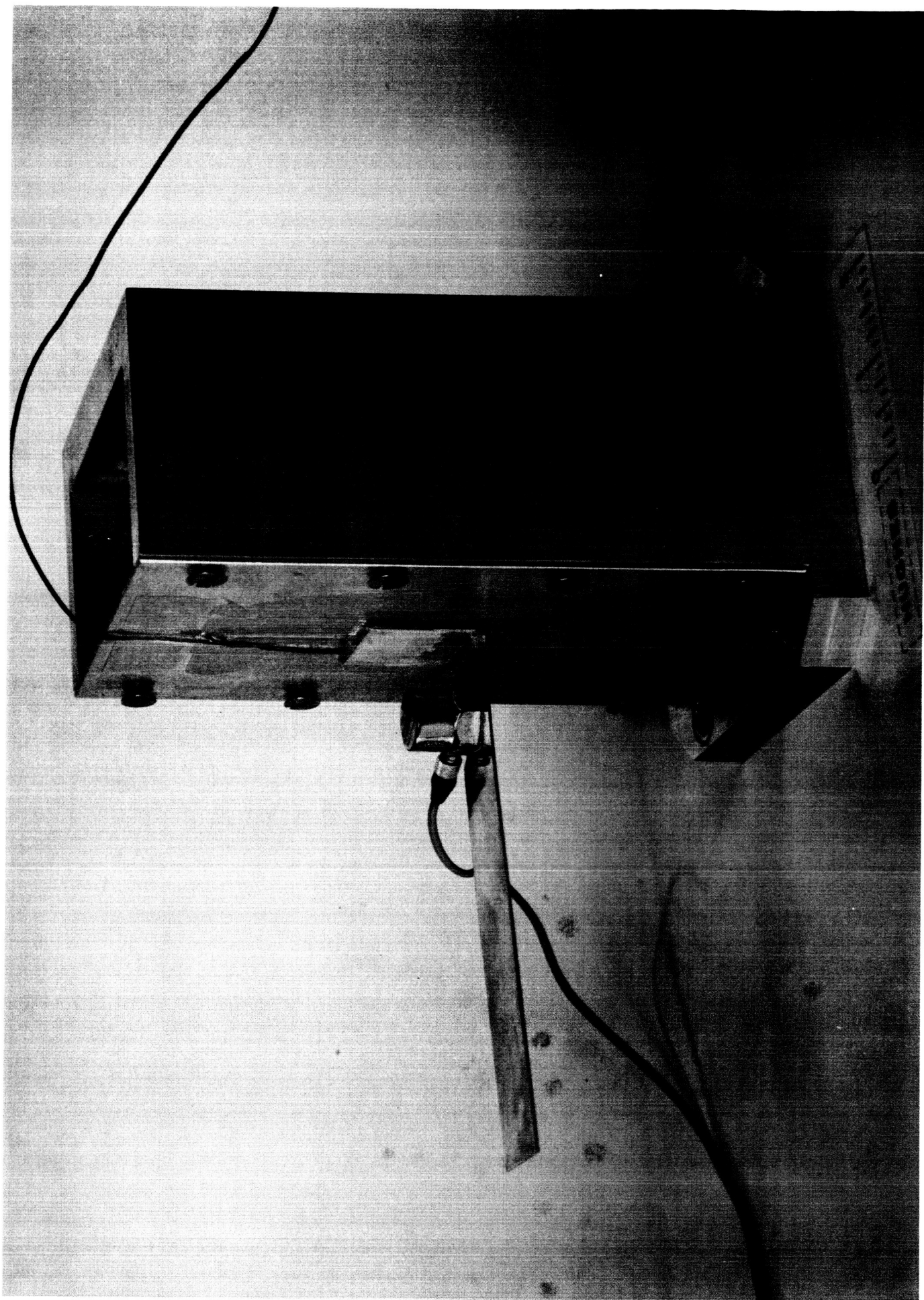


FIGURE 10

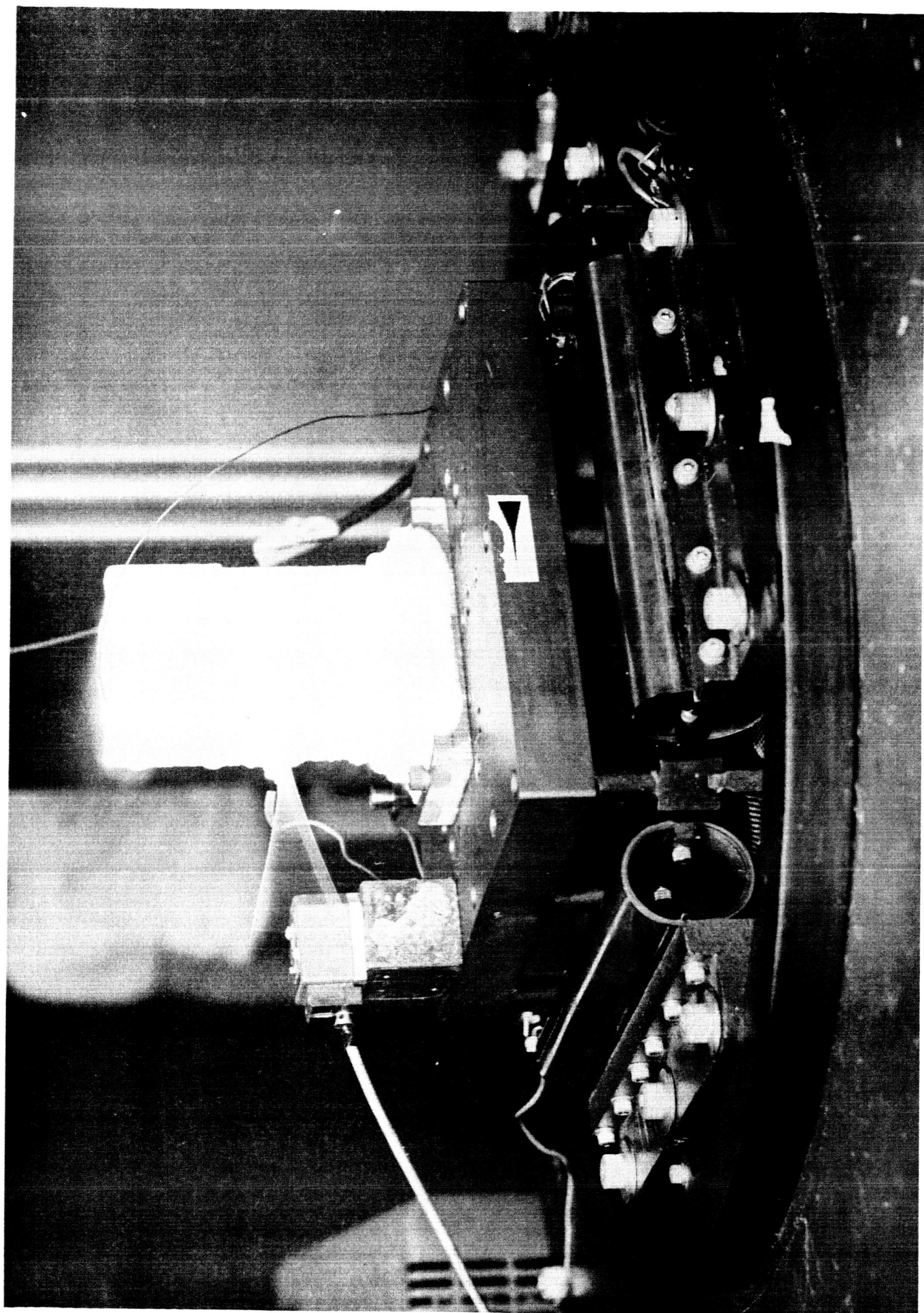


FIGURE 11



## CRYOGENIC SEALANT APPLICATION FOR DOME LOX TANK

An investigation for a cryogenic sealant application, felt by NASA to be of primary importance at this time, was carried out under this contract. This consisted of finding a material and process to seal the outer junction of the cylindrical and dome sections of liquid oxygen tanks to provide corrosion protection and a foreign particle barrier. The problem arises from the tank fabrication technique where the protective coating on the aluminum members must be removed when a welded joint is made. From this joint, the cylindrical and dome sections diverge, leaving a crevice into which metal filings and dirt lodge. The unprotected aluminum surfaces are then subject to corrosion and damage from larger foreign particles.

The sealant must provide a twofold function. It must adhere to the aluminum walls down to liquid oxygen temperature and it must keep the foreign particles away from the unprotected narrow crevice. Enough flexibility or toughness must be retained in the sealant to withstand the loads imposed by contractive movements during cool down.

Simulated tank sections were fabricated at Hughes. The crevice of one was filled with the straight Adiprene L-100 sealant (unfilled) in a way that could be done on a large tank. The surfaces were degreased by flushing and draining with methyl ethyl ketone and primed with Chemlok 607 by filling and draining. After the primer had air dried, the sealant was poured to a depth of approximately 6 inches and cured at 80°C for four hours. (This cure can be accomplished at a lower temperature, supplied by heat lamps, over a longer period of time).

The purpose of this test was to determine if the base resin would flow into the extremely small crevice near the weld. It was found that the flow was very high and it did fill areas where the gap was estimated to be about 0.005 inch. A resonance type bond tester manufactured by the Fokker Aircraft Company and using a No. 3814 transducer was used to determine if there were any void areas. Several small areas were found, indicating either areas of poor adhesion or trapped air.

When subjected to thermal shock, by plunging into liquid nitrogen, the specimens sealed with the unfilled Adiprene L-100 castor oil formulation failed at the sealant-aluminum interface. This failure occurred only at the thickest sealant section.

Additional tank sections were then sealed with the same elastomer filled with 30 parts by weight of 1/4-inch milled glass fibers. The cleaning, priming and curing were as before. Repeated immersions in liquid nitrogen did not cause failure of the sealant-metal bond, suggesting that the thermal stresses were held to a minimum by the similarities in coefficients of thermal contraction.

Peel test measurements at room temperature and at 76°K will be made, and if the strengths and modes of failure are encouraging, the material will be submitted to the sponsor for further evaluation.



## CONCLUSIONS AND FUTURE WORK

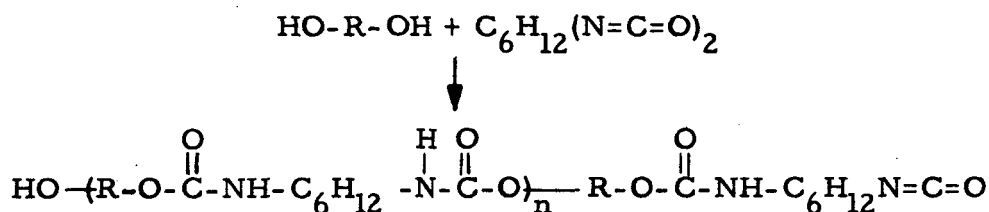
From the existing sealants and elastomers screened, Adiprene L-100, cured with castor oil, was shown to be most suitable as a cryogenic sealant. When reinforced with glass fabric, it has demonstrated an ability to resist thermal shock, bend stresses, and vibration stresses at liquid nitrogen temperature. The same material filled with glass fibers has an overall coefficient of thermal contraction, in the range of  $260^{\circ}\text{K}$  to  $80^{\circ}\text{K}$ , approximately that of aluminum. It appears to be useable for the crevice sealing of LOX dome tanks.

It is the purpose of this contract to develop a sealant in a form easily used and cured and suitable for field use. The glass fabric reinforced Adiprene "system," although showing excellent low temperature resistance, is cumbersome and requires a fairly high degree of operator skill in its application. More desirable is a sealant whose reinforcement is self-contained. To this end, the reinforcing fillers should be in the resin before application and cure. This has been tried unsuccessfully during the past year, but by using glass fibers whose finishes or sizings will provide better adhesion, and by evaluating other fibrous fillers, this problem may be solved.

Although some presently available silicone formulations may provide good low temperature resistance, when reinforced, the thermal stresses at the sealant-metal interface will be higher due to higher volume changes during cool-down. These volume changes will occur more readily during a slow cooling, allowing the polymer to crystallize.

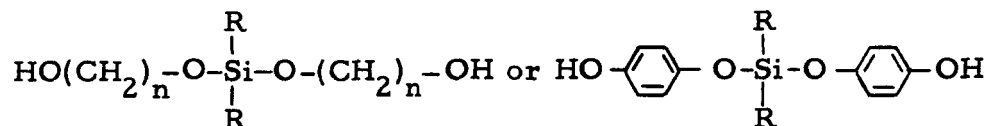
New silicone polymers are being synthesized to combine their high segmental mobility with a greater polymer disorder to reduce crystallization. Specimens using the synthesized polybutylmethylsiloxanes will be tested in bending at  $76^{\circ}\text{K}$ , and the polymer's thermal contraction properties will be studied. Other groups which will be incorporated into the basic polydimethylsiloxane chain include chloromethyl and vinyl, the latter to improve curing capabilities of the resultant silicones as well as improving cryogenic properties. Modification of the siloxane chains by cross-linking with various agents such as disilylbenzene and tetraethyl silicate will be carried out.

Polyurethanes will be prepared by the conventional reaction between a glycol and a diisocyanate:



To make the polyurethane as flexible as possible and to keep the second order transition temperature low, the monomers used in the condensation will contain carbon skeletons which are non-rigid. Thus, the diisocyanate will be one which contains the -NCO reactive groups on aliphatic chains rather than aromatic groups, and these chains may also have side groups to keep the molecules from packing tightly into a crystalline array.

The glycols will be prepared from very long chain dicarboxylic acids by reduction with lithium aluminum hydride and also from siloxyglycols such as



Other modifications will be made. Plasticizers and thixotropic fillers will be used to improve handling and application characteristics. Cure cycles will be evaluated to provide optimum results while allowing field use.

The types of compounds that have been tested and that are under consideration for extreme low temperature use are of such a composition that when immersed in liquid oxygen they will detonate under shock loading. They are therefore being considered only for immersion in non-oxidizing cryogenic fluids, or on the outside of oxidizer tanks where chances of contact are remote.

There is need, however, for a LOX safe sealant, where direct contact with the oxidizer is desired. From the known list of LOX insensitive materials, sealants will be compounded and evaluated. The list of available polymers and resins is limited, but testing need go no lower in temperature than 80°K. Work will be devoted to adapting the available LOX insensitive materials to curable sealants and testing their physical properties under liquid nitrogen. Samples of sealants will be submitted to NASA for LOX impact testing.

A definite schedule of shock and vibration tests is specified by the contracting agency. A special fixture was designed and built to accomplish the vibration testing, and the reinforced Adiprene L-100 sealant successfully passed all scheduled categories at 76°K. This test and the shock test will be repeated on the sealants that show the most promise during the program. The fixture will also be adapted for testing at 20°K.

The Fokker Bond Tester has been in use at the Hughes Aircraft Company for approximately one year as a tool in the nondestructive inspection of adhesive-bonded parts. It has been utilized on the sealed portion of a simulated LOX tank to determine the bond continuity of the Adiprene L-100 and the aluminum tank wall. Although the variable sealant thickness prevents a complete bond strength analysis from being made, void areas or the lack of a bond are quickly found. The results are encouraging, but more work will be carried out to achieve a reliable standard for various sealant thicknesses and part configurations.

The compatibility of the cured sealants and seal materials with cryogens (except liquid oxygen) and with the standard fuels and hydrocarbon test fluids will be determined by observing swelling and loss of adhesion after various periods of immersion. The ability of sealants to retain their integrity after humidity exposure will be measured after a 30-day exposure in a cabinet, the interior of which will be maintained at 165°F and 95- 100 percent relative humidity.

The best sealants will be used to fabricate O-rings and gaskets. They will be tested and compared to the materials tested by the National Bureau of Standards Cryogenic Engineering Laboratory in its work to test such materials.<sup>(42)</sup> As applicable, their abilities to provide a flange seal, their shear and compression modulus, and their tensile strengths, all at temperatures down to 20°K, will be measured.

## REFERENCES

1. Weitzel, D. H. , Robbins, R. F. , Bopp, G. R. , and Bjorklund, W. R. , National Bureau of Standards Cryogenic Laboratory, Boulder, Colorado, "Elastomers for Static Seals at Cryogenic Temperatures," Paper presented at 1960 Cryogenic Engineering Conference.

Evaluation of elastomeric O-rings for flat surface sealing.

When an ordinary O-ring seal cools, the elastomer becomes brittle at some temperature not far below room temperature, the O-ring shrinks until it loses contact with the flat surface, and the seal fails. Minimum thickness of a seal, from high compression, will result in minimum shrinkage when the seal is cooled. Samples of commercial O-rings of Vitron A, natural rubber, Neoprene, Buna N were tested and all found to be satisfactory, if a high enough compression load is applied before cool-down.

2. Tipton, F. W. et al. , "Design Data for O-rings and Similar Elastic Seals, " Boeing Airplane Co. , April 1958, WADC Tech. Rept. 56-272, Part III, AD 151181.

This was a study to gain knowledge of design data for O-rings. Functional and physical tests are described. No over-all relationship between physical property values and seal efficiency has been found. Extreme low temperature seals study initiated on the requirements to obtain a satisfactory static seal at a temperature lower than -400°F and at pressure of from 0 to 100 psi. Teflon did not exhibit brittle behavior from 4°K to 300°K. Compression tests only. Polyethylene and Kel-F did at 4°K.

The review included literature from:

1. NBS Cryogenic Eng. Lab. , Boulder
2. Ohio State Univ. , Columbus, Ohio
3. H. L. Johnson, Inc. , Columbus, Ohio
4. Lewis Flight Propulsion Laboratory of NACA, Cleveland, Ohio
5. Technical Operations, Burlington, Mass.
6. A. D. Little Inc. , Mechanical Div. , Cambridge, Mass.
7. MIT, Cambridge, Mass.

Teflon back-up improved vibration resistance. O-rings may continue to seal far below hardening point. Seal must be made at room temperature first then exposed to low temperature.

Elastomeric materials have not been used to any great extent for extremely low temperature because of brittleness. No complete evaluation is known. They must be able to compensate for a difference in thermal contraction. Organics have larger contraction than metals and may require additives.

Low temperature compression set and brittle point values did not give an indication of the usability of a seal material at reduced temperature. Young's modulus in flexure and temperature retraction curves did. It was found that type of fluid affected sealing properties, i. e. O-ring which swelled sealed better.

3. Swenson, C. A. , "Investigation of the Effect of High Pressures at Low Temperatures," September 1953, Contract DA-19-020-ORD-1891. Massachusetts Institute of Technology.

Mechanical properties of Teflon, Kel-F and Polyethylene were investigated at 40K. Only Teflon remained reasonably plastic and should be useful as a gasket material.

4. Harlow, J. E. , Murley, E. L. , Laquer, H. L. , Los Alamos, New Mexico, "Vacuum Gaskets for Use at 20°K." Advances in Cryogenic Engineering, Vol. 5, Plenum Press (Proc. of the 1959 Cryogenic Engineering Conference, University of California, September 2-4, 1959).

Teflon O-rings were tested successfully in the same way as Weitzel and Robbins and NBS, i. e. flat plate gasketing against vacuum at 20°K. The material must be highly compressed at room temperature, however, to retain the seal.

5. Sabanas, M. and Iwatsuki, F. , "Composite Seal Materials", Armour Research Foundation. Paper presented at the 6th JANAF conference on Elastomer Research and Development, October 1960.

In this program seals were developed having a combination of the thermal properties of metal and the mechanical properties of elastomers. Sintered metal fibers were impregnated with phosphonitrilic chloride,

SR32 silicone resin slurry, Teflon, potassium silicate, silica, zirconia, and various soft metal fillers.

6. Weitzel, D. H., Robbins, R. F., and Herring, R. N, "Elastomeric Seals and Materials at Cryogenic Temperatures." NBS Report 6775, National Bureau of Standards Cryogenic Laboratory, Boulder, Colorado, June 1, 1961.

Static Seals - simple flat flange design is being substituted for the tongue and groove design. The metallic seals developed by Armour Research were tested in this portion of their program.

Properties of Elastomers - a continuation of compression studies on O-rings made from Viton A and Teflon.

7. Lucas and Hernandez - Reveiw of Scientific Instruments, Vol. 30, No. 10 941-942, Oct. 1959, "Inflatable Gasket for the 72 inch Bubble Chamber."

The gasket evaluated for sealing the chamber, at liquid hydrogen temperatures, was indium wire on an inflatable stainless steel member. This proved to be quite satisfactory.

8. Braun, D., and Crockwell, G. W. - Personal Contact. Silicone Division, Union Carbide and Carbon Corp. - Tonawanda, New York.

9. Lieb, J. H. and Mowers, R., "Problems in Evaluating and Testing Plastics, "Materials in Design Engineering Special Report No. 185, July, 1961.

Outstanding among the limited number of plastic retaining some ductility at ultra-low temperatures are the fluorocarbons, e.g., TFE, Teflon, FEP Teflon, and CFE (Kel-F).

At -320°F fluorocarbons of low crystallinity, high amorphous content, are stronger and more ductile than highly crystalline materials.

10. Atlantic Research Corp., "The Development of Fuel-Resistant Arctic Rubber, " Feb. 1960.

Terpolymers containing ester, amide and urethane groups as the components of the polymer molecule were synthesized to obtain rubbers for use over temperature range -100°F to +150°F. N-substituted dialkanolamines, diacids, triethanolamine, and diisocyanates were used as monomers to produce polymer chains having irregularly spaced ester,

amide, and urethane group. Disruption of orderly array of polymer units reduces or prevents crystallization and improves flexibility at low temperatures.

11. Bennet, B., Stickney, P. B., Heiligman, R. G., "Literature Survey of the Melting and Glass Transitions of Elastomers, Battelle Memorial Institute, Contract No. DA-20-089-ORD-16702, January 1956.

<u>Polysiloxanes</u>	<u>Crystallization Temp. °C</u>
G. E. Silicone rubber 9979G	-60 to -67
D. C. Silastic X-6160	-60 to -67
D. C. Silastic 250	-75 to -85
D. C. Silastic X-6073	none between -180 and 100

Polysiloxanes glass temperature appear to be unaffected by the addition of fillers or by vulcanization. A copolymer (siloxane) reportedly containing 5 mole percent of phenyl groups is non crystallizable.

#### Highly Fluorinated Elastomers

Polymers of 2-fluorobutadienes did not crystallize when stretched at low temperature. Kel-F elastomers (methylene groups) are amorphous down to -40°C. Crystallinity is shown on stretching at room temperature.

12. Johnson, V. J., editor, "Compendium of the Properties of Materials at Low Temperature," Cryogenics Laboratory, National Bureau of Standards, Boulder, Colorado, WADC Report TR60-56.

In phase II of this work, specific heat and enthalpy curves, at cryogenic temperatures, are given for polyvinyl alcohol, Glyptal, a Bakelite varnish, polyethylene, molded Teflon, natural rubber hydrocarbon, and GRS rubber. The T<sub>g</sub> for the natural rubber was given as 200°K, and 212°K for the GRS.

13. Carey, J. E. -Paper presented at the SPE Symposium on Epoxy Resins, Nov. 1956, "Thermal Expansion of Filled Epoxy Resins,"

A comparison was given of the coefficients of thermal expansion of various epoxy resin-filler combinations. The best inorganic filler for the coefficient reduction of an organic system, approaching that of



aluminum, is a lithium aluminum silicate designated as Stupalith 2410, manufactured by the Carborundum Corporation.

14. Gray, V. H., and Gelder, T. F., NASA, Lewis Research Center, Cleveland, Ohio, "Externally Bonded and Sealed Insulation for Liquid-Hydrogen-Fueled Rocket Tanks." Advances in Cryogenic Engineering-Vol. 5, Plenum Press. (Proc. of the 1959 Cryogenic Engineering Conference, University of California, Sept. 2-4, 1959.)

The main problem of bonding insulation directly to metal tanks is the shrinkage of the tank when it is chilled with cryogenic liquid. It has been shown that epoxy resin reinforced with glass fibers nearly matches the contraction rate of aluminum, and that it is a strong adhesive down to low temperatures.

Surface preparation of the metal greatly effects the bond strength, ranging from about 1100 psi for "degrease only" to more than 5000 psi for vapor blast. (Epon 820 with one layer 181 glass cloth).

As sealants over insulation, 1 mil thick Mylar and sheet Saran were effective. Two others promising were Neoprene (as used on radomes) and aluminum-filled lacquer (used on blimps.)

15. Griffin, W. R., "Elastomer Research at Wright Air Development Division," Nonmetallic Materials Laboratory, Materials Central, Paper presented at the 6th JANAF Conference on Elastomer Research and Development, October, 1960.

Fluoracrylate elastomers such as Fluororubber 1F4 and 2F4 have poor low temperature flexibility. Silastic LS-53 and the newer LS-63 have good low temperature flexibility.

Also of interest are Fluorel and Viton elastomers. Viton A and A-HV, although having a slightly higher brittle point than Viton B, have a return of rubbery characteristics at a temperature below that of Viton B. Thus, Viton A and A-HV appear preferable for low temperature dynamic applications where elastic properties are required, and Viton B for low temperature static applications where leather-like flexibility can be tolerated.

Cyanosilicones and perfluoronitroso elastomers have extreme low temperature flexibility.

16. Kilbourne, F. L., Connecticut Hard Rubber Co., "Development of Silicone Rubbers for use at Temperatures Down to -100°F, Nov. 1952.

Use of reinforcing fillers for G. E. SE-76 silicone rubber.

G. S. Silica was found to be good as a simultaneous curing and reinforcing pigment. It is better with a small amount of  $\text{Bz}_2\text{O}_2$  added. 15-25% volume loading gave best rubber stocks. The best cure is at 300° to 350°F. Brittle points are well below -80°F.

17. Dombrow, B. A., "Polyurethanes, "Reinhold Pub. Corp., 1957.

Adiprene C manufactured by Du Pont will not become brittle until temperatures below -95°F are reached. (Adiprene L-100 is a newer material and is reputed to have somewhat better low temperature properties.)

The best potting recipe for low temperature use involves castor oil, tolylene diisocyanate and 2-ethyl hexanediol-1, 3 cured with a small quantity of ditertiary butoxydiamine silane.

18. Reichel, R. C., Armour Research Foundation of Illinois Institute of Technology, "Evaluation and Development of Extreme Low Temperature Insulating Materials."

A modified polyurethane foam successfully passed a liquid hydrogen thermal shock test when it was foamed around a wooden plug. Because of this work which was directed toward development of, and insulation for  $\text{LH}_2$ , further modification might lend utility as an elastomer for sealant applications.

19. Frost, W. M. - Paper presented before 1959 Cryogenic Engineering Conference, "The Strength of Ten Structural Adhesives at Temperatures Down to 20°K."

Epoxy-phenolic and filled epoxy adhesives, such as Shell's Epon 422 and Minnesota Mining and Manufacturing's EC-1469, performed best at cryogenic temperatures. Materials of other composition, notably the vinyl or rubber modified phenolics, had sizeable strength reductions. The vinyl-phenolic and epoxy adhesives maintain fairly constant shear strengths under shock loading as high as  $10^8$  psi per minute.

20. Mc Clintock and Hiza - Modern Plastics, June 1958, "Epoxy Resins as Cryogenic Structural Adhesives."

In studying the strengths of epoxy based adhesives bonded to copper down to 20°K, bonds were formed which were even stronger at 77°K than they were at room temperature. Glass fibers were used to match the coefficients of thermal contraction.

21. Berenbaum, M. -Personal Contact, Chemical Division, Thiokol Chemical Corp., Trenton, New Jersey.

22. Viohl, P. and Haxo, H. -Personal Contact, U. S. Rubber Corp., Research Laboratories - Wayne, New Jersey.

23. Radi, L. J., Britt, N. G., Ind. and Engineering Chem. Vol. 46, pp. 2439, Nov. 1954, "Fundamental Low Temperature Retraction Studies of Natural and Synthetic Elastomers."

This paper presented a procedure to measure the degree of crystallinity and plot transition points by measuring the retraction rates of elastomers held at specific low temperatures (down to --70°C).

24. Schwarz, E. G., "The Micro-Compounding and Evaluation of Rubber-Like Polymers," WADC Technical Report 57-247, July 1957.

A qualitative low temperature screening may be performed on the uncompounded polymer itself, i. e., by immersing the polymer in ice water and then progressively colder media. More refined techniques for measuring low temperature flexibility of cured elastomers, and even polymer samples with enough rigidity to be sheeted, include those of the Gehman Torsional, Temperature Retraction, and Brittle Point Tests, as outlined in the ASTM Standards on Rubber Products.

25. Jenkins, T. C. and Logan, S. E., "Propellant Static Seal Development in Project Hermes," Nov. 1954, General Electric Company, AD 50626.

An extensive study of O-ring type sealing method was carried out. The most satisfactory was a static seal for liquid oxygen that was temperature compensating.

Type W Neoprene with P33 carbonblack filler performed satisfactorily.

Type N Neoprene with TiO<sub>2</sub> filler may be as good or better

26. Sinnott, K. M., Journal of Applied Physics, Vol. 29, No. 10, 1433-1437, Oct. 1958, "Apparatus for the Measurement of Shear Modulus and Internal Friction Between 4.2 and 100°K. "

An apparatus has been constructed to measure the shear modulus and logarithmic decrement of polymers from 4.2 to 100°K. The apparatus consists of a small torsion pendulum suspended on a rigid support at the bottom of a large glass Dewar vessel. After cooling to 4.2°K with liquid helium, the pendulum warms up at an initial rate of 0.1° per minute. Torsional oscillations of the pendulum are excited electrically and recorded photographically. The estimated accuracy of the modulus and logarithmic decrement is ±5.0%.

Measurements of the shear modulus and logarithmic decrement have been made from 4.2 to 100°K on a series of tetrafluoroethylene-hexafluoropropylene copolymers.

27. Blum, G. W., "Sealing Compounds," Case Institute of Tech., September 1953, Contract DA-33-019-ORD-940, AD 17523.

The following mastic materials were tested to MIL-S-11030A and MIL-S-11031A:

1. rubber-wax-rosin esters
2. silicones and Silastics
3. Hypalon S-2
4. polybutadienes
5. organic greases
6. silicon alkyds

The mathematical relationship which exist between variations of shear stress with rate of shear, as functions of the composition of the mastic materials for both rotary and static sealant materials were derived. The expression is  $[\log P = S \log V = \log C]$  or  $P = CV^S$  where P is the pressure required, V is the flow rate through a fixed orifice in inches per second, C is the intercept, and S is the slope of the lines.

A survey of the literature showed little treatment of the subject (180° to -80°C). Gelled silicone oils are not suitable as mastics. Chlorosulfonated polyethylene type polymers cure too readily, and once cured are useless as mastics. Silicone alkyds are not suitable for low

temperature sealants. Rubber-wax-resins have unsatisfactory low temperature properties.

28. Lucas, W.R. and Riehl, W.A., "An Instrument for the Determination of Impact Sensitivity of Materials in Contact with Liquid Oxygen," 15 October 1958, Engineering Materials Branch, Structures and Mechanics Laboratory, Development Operations Division, ABMA, Redstone Arsenal, Alabama, Report DSN-TR-2-58.

This report discussed the development of an impact tester. It compares several proprietary sealants vs. Oxyseal, a commercial sealant consisting primarily of a mixture of graphite and a chlorinated biphenyl, known to be insensitive to liquid oxygen.

The gasket materials tested were:

Allpox 5364A, 5408A 5408B, 5409B, 7700, 9662, 9670

Johns Manville 76 and 60

29. Liska, J.W., "Effect of Low Temperatures on Young's Modulus of Elastomers," Industrial and Engineering Chemistry, Vol. 36, p. 40 (1944).

Data are presented showing the manner in which Young's modulus of both natural and synthetic rubber varies with temperature in the range 0° to -60°C. Stocks having relatively high moduli at a given low temperature sometimes have very low brittle point temperatures.

30. Dukes, W.A., "Improved Luting Compositions- Part IV," July 1955, Explosives Research and Development Establishment (Gt. Britain).

R. D. 1287, a proprietary sealant, was developed but was only tested and felt to be serviceable down to -80°F.

31. Stegner, J.A., "Evaluation of a Commercially Available Primer with Respect to Improving Adhesion of MIL-S-8516B Sealing Compound to Various Materials," Aeronautical Materials Lab., NAMC, Philadelphia, AD 156465.

3M's EC776 primer did improve adhesion where contamination by silicon grease and petroleum base oils was present.

32. Snider, J.M. and Hirosawa, F., Coast Pro-Seal Manufacturing Co., "Development of Integral Fuel Tank Sealant Compound" May 1954, WADC Tech Report 53-450.

Attempts made to develop a sealing compound from materials other than polysulfide polymers. Copolymers of ethyl acrylate and allyl glycidyl ether poor in aromatic fuel resistance and low temperature flexibility. Polymers cured to elastomeric products by reaction of amine curing agents with epoxy groups had good high temperature properties but poor low temperature flexibility. Liquid polymers of a polyester type were prepared from mercaptoacetic acid and made sensitive to oxidation curing reactions by heat treatment. Had excellent resistance to aromatic fuels and were considered promising.

A polyester prepared by condensing methyl diethanolamine, a mixture of C<sub>10</sub> diacids and triethanolamine, when chain extended and X-linked with hexamethylene diisocyanate yielded an elastomer which was flexible over the temperature range of -100°F to +150°F. The cured polymer deteriorates after prolonged aging under ambient conditions, i. e., the polymer loses tensile strength and becomes soft and tacky. Proper compounding should eliminate this tendency.

33. Post, H. W. and Schwartz, W. T., Jr., University of Buffalo, "The Development of Chemically Resistant Rubbers from Semi-Organics for Use at Extreme Low Temperatures," February 1961.

At first they prepared some polymeric siloxanes in which an occasional silicon atom is replaced by that of titanium. Such were inferior to those already developed. A completely new series of polymers based on the preparation of bis (vinylcyclopentadienyl) titanium dichloride and its copolymerization with suitable monomers are under development.

34. Steele, D. V. and Timmius, A. R., U. S. Naval Ordnance White Oak, Maryland, "O-Ring Materials for Naval Ordnance Applications," November 1960.

Linear ZB-70 silicone O-rings are suitable for static seals and are resilient at temperatures as low as -100°F.

35. Lichtman, J. Z., Material Lab., New York Naval Shipyard, Brooklyn, "Investigation of the Applicability of the Sealing Pressure Test Apparatus to the Low Temperature Evaluation of Natural and Synthetic Elastomers," October 1953.

The apparatus they developed was unsatisfactory for the determinations of either sealing pressure or follow-up on decreasing the specimen indentation. Materials tested were Neoprene, Buna S, Perbunan 26, Hevea, Butyl and Thiokol FA.

36. Beaman, R. G., J. Polymer Sci., Vol. 9, No. 5, pp. 471, Nov. 1952.

The Glass Transition Point of Some Chemicals

	Tg's (°K)
n-propyl alcohol	93
ethyl alcohol	93
polydimethylsiloxane (linear polymer)	150
glycerol	185
phosphorus	196
dl-lactic acid	200
natural rubber (linear polymer)	200
poly (ethylene adipate) "	203
poly (tetramethylene Sebacate) "	216
sodium thiosulfate	230

37. Weir, C. E., Laser, W. H., and Wood, L. A., "Crystallization and Glass Transition Temperatures in Silicone Rubber" Journal of Research, National Bureau of Standards, Vol. 44, April 1950.

38. Simha, R., "On a General Relation Involving the Glass Temperature and Coefficients of Expansion of Polymers," paper presented before the Pacific Southwest Regional Meeting, American Chemical Soc., Dec. 1961.

39. Carey, J. E., "Thermal Expansion of Filled Epoxy Resins," paper presented at the SPE Symposium on Epoxy Resins, Nov. 1956.

40. Klebanskii, A. L., Fikhtengol'ts, V. S., and Karlin, A. V., J. Gen. Chem., Moscow, Vol. 27, pp. 3321, 1957.

41. Kidwell, A. S., U. S. Patent 2,736,720, 1956.

42. Weitzel, D. H., et al., "Elastomeric Seals and Materials at Cryogenic Temperatures," ASD report TDR-62-31.

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